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Reactions of Indole and Its Derivatives with Cotarnine. Rearrangement of 5-(1-Indolyl)-4-methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinolines

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Abstract—A synthetic route to compounds of the indolyltetrahydroisoquinoline series was developed on the basis of the reaction of cotarnine with indole derivatives. Aminoalkylation of indole and its derivatives with cotarnine occurs regioselectively at the nitrogen atom of the indole fragment to give the corresponding 5-(1-indolyl)-4-methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinolines. The products were found to undergo rearrangement into isomeric 5-(3-indolyl)-4-methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinolines which constitute a new class of indolyltetrahydroisoquinoline systems.

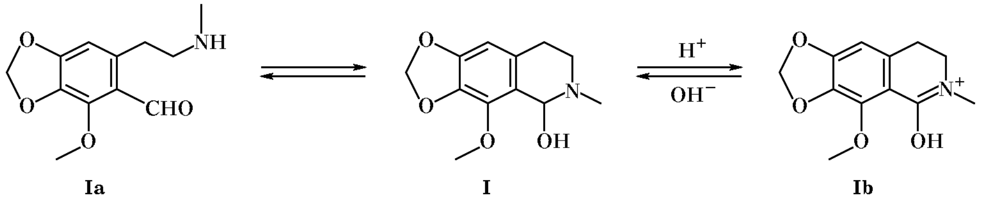
4-Methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline (**I**, cotarnine) is a natural tautomeric pseudobase which is known to react with some CH and NH acids with formation of so-called dihydrocotarnyl derivatives [1, 2]. These compounds attract interest as potential biologically active substances structurally related (to more or less extent) to plant alkaloids of the isoquinoline series [3].

The reaction of cotarnine with indole (**II**) and its derivatives is among the most interesting and at the same time poorly studied aspects of the chemistry of this compound. Such reactions open the way to compounds of the indolylisoquinoline series. Published data on this topic are very limited. Hope and Robinson [4] obtained the corresponding *N*-dihydrocotarnyl derivatives from isatin and 2-methylindole (**III**), while reactions of cotarnine with unsubstituted indole and other indole derivatives were not studied. In continuation of our works [5] on the synthesis of new analogs of isoquinoline alkaloids, we examined reactions of cotarnine with indole (**II**) and some its derivatives.

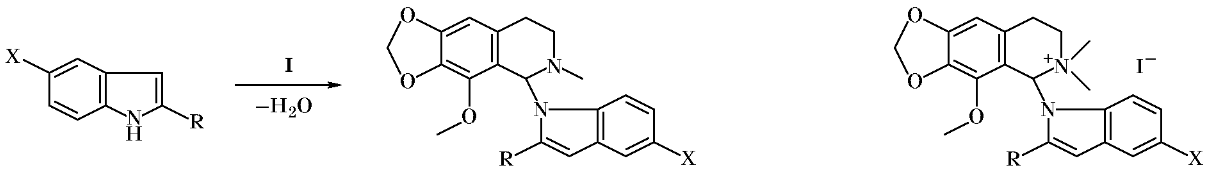
Reactions of cotarnine with nucleophilic substrates could involve intermediate formation of either cation **Ib** or open tautomeric form **Ia** (Scheme 1) [6]. As a rule, such reactions are treated as a particular case of aminoalkylation [1], and the products are classed with Mannich bases.

We have found that cotarnine (**I**) reacts with indole (**II**) in methanolic solution to give only one product, 5-(1-indolyl)-4-methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline (**IV**, 1-dihydrocotarnylindole) (Scheme 2). Its structure was proved by the data of ^{1}H NMR spectroscopy (Table 1) and mass spectrometry. Hence the alkylation of indole with cotarnine under the given conditions occurs selectively at the nitrogen atom. According to the TLC and ^{1}H NMR data, no alkylation product at C^3 was formed. This result contradicts the known relations holding in the Mannich reaction with indole derivatives which usually react at position *3* [7, 8]. Up to now, the only reliable example of N-aminoalkylation of indole was described by Swaminathan and Narasimhan [9], who

Scheme 1.



Scheme 2.



II, III, VI, VII **IV, VIII–X** **V, XI–XIII**

II, **IV**, **V**, R = X = H; **III**, **VIII**, **XI**, R = CH_3, X = H; **VI**, **IX**, **XII**, R = H, X = Br; **VII**, **X**, **XIII**, R = H, X = OCH_3.

performed a heterophase synthesis of N-isoharmine and its analogs; however, the products were not isolated in the pure state because of their instability.

1-Dihydrocotarnylindole (**IV**) undergoes hydrolysis to initial compounds **I** and **II** by the action of acids; however, in the absence of acids compound **IV** is stable up to 170°C, in contrast to acyclic *N*-aminoalkyl derivatives of indole [9] which are unstable even at room temperature. Probably, the relatively high hydrolytic stability of **IV** is explained by steric factor: the presence of a bulky dihydrocotarnyl group which is difficult to depart. Quaternary ammonium salt **V** derived from **IV** was also stable: it decomposed only on heating above 190°C.

The reactions of cotarnine with 2-methylindole (**III**), 5-bromoindole (**VI**), and 5-methoxyindole (**VII**) in MeOH gave the corresponding derivatives **VIII**–**X** which were converted into quaternary salts **XI**–**XIII**. All these products are stable in the crystalline state and in neutral solution, and they decompose into initial compounds on treatment with acids.

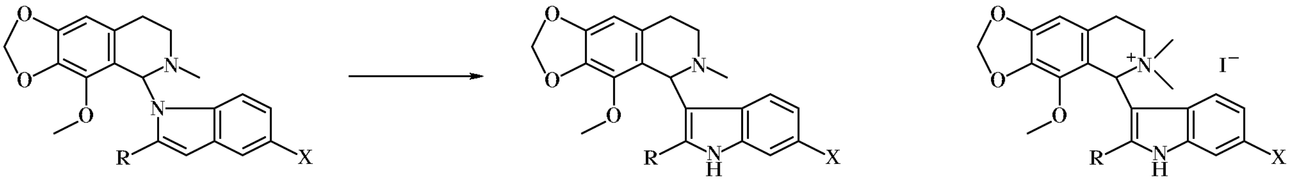
Thus in the reactions of cotarnine with both unsubstituted indole **II** and its derivatives **III**, **VI**, and **VII** aminoalkylation of the indole fragment occurs selectively at the nitrogen atom, yielding stable N-substituted indolyltetrahydroisoquinoline Mannich bases.

By contrast, 1-methylindole failed to react with cotarnine even on heating in boiling alcohol for 24 h. This result suggests that cotarnine, unlike classical Mannich reagents (such as formaldehyde–secondary amine), is incapable of reacting directly at C^3 of N-substituted indoles.

We have found that under certain conditions 1-dihydrocotarnylindoles can be transformed into 3-dihydrocotarnylindoles. By heating compound **IV** in aqueous alkali we obtained a new substance whose molecular weight (according to the MS data) was the same as that of the initial compound, but it had different spectral parameters. The ^{1}H NMR spectrum of isomerization product **XIV** (see figure and Table 1) contained a downfield signal from NH proton, the indole 3-H signal was absent, and the signal from 2-H of the pyrrole ring was a singlet. On the basis of these data, product **XIV** was assigned the structure of 5-(3-indolyl)-4-methoxy-6-methyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-*g*]isoquinoline (3-dihydrocotarnylindole). The ^{13}C NMR spectrum of **XIV** was also consistent with the assumed structure. The discovered rearrangement opens the way to 3-dihydrocotarnylindoles which constitute previously unknown class of indolyltetrahydroisoquinoline systems.

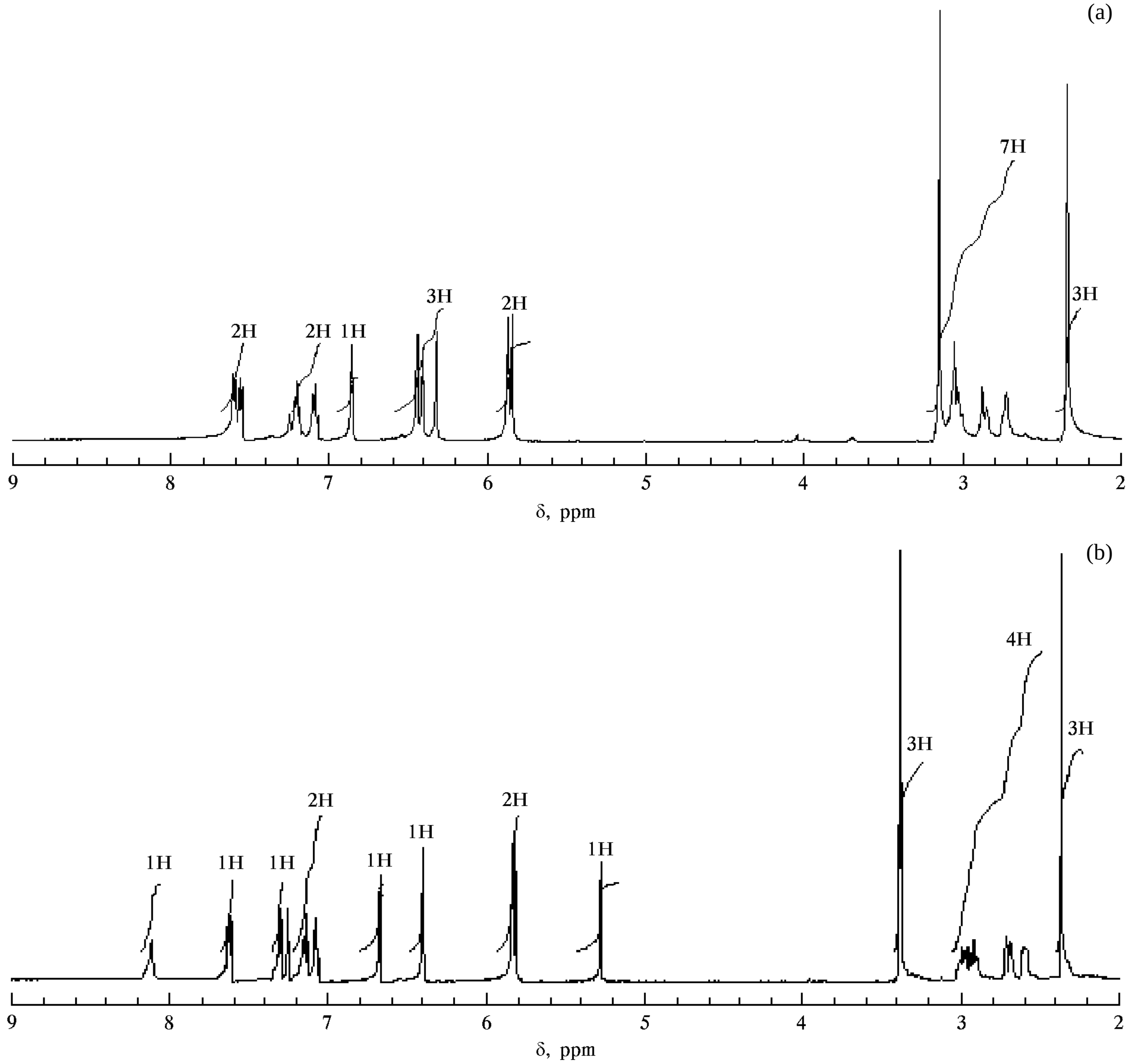
The isomerization of substituted 1-dihydrocotarnylindoles **VIII**–**X** gave the corresponding 3-dihydrocotarnylindoles **XV**–**XVII** in 60–80% yield. Compounds **XIV**–**XVII** have higher melting points and are more thermally stable (up to 200°C and higher) than their *N*-substituted isomers. In addition, they are more resistant to hydrolysis. Compounds **XIV**–**XVII** do not decompose during chromatographic treatment; they remain intact in the presence of strong acids

Scheme 3.



IV, VIII–X **XIV–XVII** **XVIII–XXI**

XIV, **XVIII**, R = X = H; **XV**, **XIX**, R = CH_3, X = H; **XVI**, **XX**, R = H, X = Br; **X**, **XIII**, R = H, X = OCH_3.



^{1}H NMR spectra ($CDCl_3$) of (a) compound **IV** and (b) its isomerization product **XIV**.

(the corresponding salts are formed). Qauternary salts **XVIII**–**XXI** derived therefrom are also more stable than the corresponding N-isomers **V** and **XI**–**XIII**.

The mechanism of rearrangement of 1-dihydrocotarnylindoles into 3-substituted isomers still remains unclear. Probably, this reaction is an example of a new 1–3-sigmatropic rearrangement in the indole series. The rate of the rearrangement is the highest in aqueous alcohol; the reaction in anhydrous alcohol is much slower, while on heating in anhydrous aprotic solvents (e.g., in bromobenzene) or without a solvent 1-dihydrocotarnylindole **IV** undergoes decomposition, and no isomer **XIV** is formed. These findings may be regarded as an indirect evidence that the rearrangement of 1-dihydrocotarnylindoles involves a polar or ionic transition state which could be formed only in strongly polar solvating medium.

To conclude, it should be noted that further studies of the discovered rearrangement of 1-dihydrocotarnylindoles, apart from the direct interest, may be useful from the viewpoint of refinement of the mechanisms of known aminoalkylation reactions of indole and its derivatives.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker AM-500 spectrometer (500 MHz) in $CDCl_3$ and DMSO-d_6. The mass spectra (70 eV) were obtained on an MKh-1303 instrument with direct sample

Table 1. Chemical shifts δ (ppm) and spin–spin coupling constants *J* (Hz) in the ^{1}H NMR spectra of compounds **IV**, **V**, and **VIII**–**XXI**

Comp. no.	Solvent	Indole fragment						
		NH	2-R	3-H	4-H	5-R	6-H	7-H
IV	$CDCl_3$	–	6.85 d, *J* = 3.4	6.41 d, *J* = 3.4	7.55 d, *J* = 8.2	7.09 d.d	7.19 d.d	7.59 d, *J* = 7.0
V	DMSO-d_6	–	6.98 d, *J* = 3.5	6.57 d, *J* = 3.5	7.57 d, *J* = 8.2	7.17 d.d	7.33 d.d	8.31 d, *J* = 8.2
VIII	$CDCl_3$	–	2.36 s, 3H, CH_3	6.68 s	6.70 d, *J* = 8.4	6.82 d.d	6.99 d.d	7.82 d, *J* = 8.4
IX	DMSO-d_6	–	7.05 d, *J* = 3.5	6.55 d, *J* = 3.5	7.72 s	–	7.43 d, *J* = 7.1	8.35 d, *J* = 7.1
X	$CDCl_3$	–	6.78 d, *J* = 3.6	6.28 d, *J* = 3.6	7.00 s	3.83 s, 3H, OCH_3	6.81 d, *J* = 8.4	7.37 d, *J* = 8.4
XI	DMSO-d_6	–	2.36 s, 3H, CH_3	6.70 s	7.52 d, *J* = 8.2	7.05 d.d	7.26 d.d	8.22 d, *J* = 7.5
XII	DMSO-d_6	–	7.07 d, *J* = 3.3	6.57 d, *J* = 3.3	7.73 s	–	7.44 d, *J* = 9.0	8.36 d, *J* = 9.0
XIII	DMSO-d_6	–	6.83 d, *J* = 3.6	6.35 d, *J* = 3.6	7.06 s	3.94 s, 3H, OCH_3	6.74 d, *J* = 8.8	7.13 d, *J* = 8.8
XIV	$CDCl_3$	8.11	6.68 s	–	7.30 d	7.08 d.d	7.13 d.d	7.62 d
XV	$CDCl_3$	7.86	2.36 s, 3H, CH_3	–	7.13 d, *J* = 8.2	6.88 d.d	6.97 d.d	7.13 d, *J* = 8.2
XVI	DMSO-d_6	10.78	6.61 s	–	7.64 s	–	7.07 d, *J* = 7.6	7.22 d, *J* = 7.6
XVII	$CDCl_3$	8.19	6.64 s	–	6.99 s	3.83 s, 3H, OCH_3	6.79 d, *J* = 9.4	7.15 d, *J* = 9.4
XVIII	DMSO-d_6	11.46	7.11 s	–	7.41 d, *J* = 8.2	7.05 br.s	7.05 br.s	8.10 br.s
XIX	$CDCl_3$	10.35	2.75 s, 3H, CH_3	–	6.66 d, *J* = 8.4	6.83 d.d	6.95 d.d	7.48 d, *J* = 8.4
XX	DMSO-d_6	11.66	7.10 br.s	–	8.40 br.s	–	7.22 d, *J* = 8.2	7.37 d, *J* = 8.2
XXI	DMSO-d_6	11.28	6.98 br.s	–	7.65 br.s	3.90 br.s, 3H, OCH_3	6.81 br.s	7.28 d, *J* = 9.9

Comp. no.	Tetrahydroisoquinoline fragment						
	NCH_3	OCH_3	OCH_2O	$ArCH_2$	NCH_2	NCH	H_{arom}
IV	2.34	3.15	5.85 d, *J* = 7.9	2.60 m, 2.73 m	3.04 m	6.32 s	6.44 s
V	3.09, 3.28 (3H + 3H)	3.46	6.01 d, *J* = 4.7	3.38 m	3.76 m, 3.84 m (1H + 1H)	7.04 s	6.69 s
VIII	2.35	3.19	5.89 d, *J* = 8.0	2.55 m, 2.70 m	3.10 m	6.25 s	6.43 s
IX	2.93	3.47	6.02 d, *J* = 4.8	3.30–3.42 m	3.75 m, 3.87 m (1H + 1H)	7.03 s	6.55 s
X	2.31	3.14	5.86 d, *J* = 9.1	2.59 m, 2.70 m (1H + 1H)	3.03 m	6.20 s	6.40 s

Table 1. (Contd.)

Comp. no.	Tetrahydroisoquinoline fragment						
	NCH_3	OCH_3	OCH_2O	$ArCH_2$	NCH_2	NCH	H_{arom}
XI	3.04, 3.38 (3H + 3H)	3.44	6.00 d, *J* = 12.0	3.37 m	3.69–3.99 m	6.96 br.s	6.59 s
XII	2.93, 3.46 (3H + 3H)	3.36	6.03 d, *J* = 5.2	3.35 m	3.76 m, 3.87 m (1H + 1H)	7.03 s	6.68 s
XIII	3.02, 3.33 (3H + 3H)	3.42	5.98 d, *J* = 11.0	3.36–3.49 m	3.64 m, 3.85 m (1H + 1H)	7.01 s	6.42 s
XIV	2.39	3.40	5.83 d, *J* = 9.6	2.64 m, 2.73 m (1H + 1H)	2.93–3.04 m	5.29 s	6.40 s
XV	2.33	3.20	5.73 s, 5.86 s (1H + 1H)	2.63 m, 2.96 m (1H + 1H)	2.99–3.07 m	5.00 s	6.41 s
XVI	2.31	3.45	5.86 d, *J* = 3.6	2.48–2.62 m	2.87 m	5.04 s	6.34 s
XVII	2.39	3.40	5.83 d, *J* = 11.2	2.63 m, 2.72 m (1H + 1H)	2.92–3.03 m	5.22 s	6.40 s
XVIII	3.00, 3.37 (3H + 3H)	3.42	5.94 s	3.29 m	3.68 m	6.16 s	6.58 s
XIX	2.99, 3.48 (3H + 3H)	3.46	5.79 s, 5.86 s (1H + 1H)	3.35 m	3.63 m, 3.98 m (1H + 1H)	5.54 s	6.49 s
XX	3.02, 3.37 (3H + 3H)	3.46	5.95 s	3.26 m	3.72 m	6.17 s	6.58 s
XXI	3.07, 3.41 (3H + 3H)	3.47	5.96 s	3.33 m	3.75 m	6.17 s	6.58 s

Table 2. Yields, melting points, and elemental analyses of compounds **IV**, **V**, and **VIII–XXI**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	H	Hlg	N		C	H	Hlg	N
IV	90	142–143	71.29	6.04	–	8.35	$C_{20}H_{20}N_2O_3$	71.41	5.99	–	8.37
V	95	190–200[a]	52.77	4.86	26.48	5.85	$C_{21}H_{23}IN_2O_3$	52.74	4.85	26.53	5.86
VIII	45	97–98	71.60	6.39	–	7.92	$C_{21}H_{22}N_2O_3$	71.99	6.33	–	7.99
IX	88	131–132	55.78	4.37	18.46	6.41	$C_{20}H_{19}BrN_2O_3$	55.96	4.46	18.61	6.53
X	52	122–123	68.44	6.12	–	7.53	$C_{21}H_{22}N_2O_4$	68.84	6.05	–	7.65
XI	87	190–200[a]	53.31	5.24	25.42	5.60	$C_{22}H_{25}IN_2O_3$	53.67	5.12	25.77	5.69
XII	83	200–210[a]	45.09	4.11	36.88	4.99	$C_{21}H_{22}BrIN_2O_3$	45.27	3.98	37.11	5.03
XIII	89	195–200[a]	52.32	4.98	24.71	5.56	$C_{22}H_{25}IN_2O_4$	51.98	4.96	24.96	5.51
XIV	71	204–205	71.23	5.94	–	8.32	$C_{20}H_{20}N_2O_3$	71.41	5.99	–	8.37
XV	66	155–156	71.56	6.15	–	7.91	$C_{21}H_{22}N_2O_3$	71.99	6.33	–	7.99
XVI	79	244–245	56.12	4.50	18.49	6.50	$C_{20}H_{19}BrN_2O_3$	55.96	4.46	18.61	6.53
XVII	83	199–200	68.55	6.17	–	7.53	$C_{21}H_{22}N_2O_4$	68.84	6.05	–	7.65
XVIII	92	200–210[a]	53.02	4.91	26.09	5.88	$C_{21}H_{23}IN_2O_3$	52.74	4.85	26.53	5.86
XIX	90	200–210[a]	53.94	5.27	25.28	5.70	$C_{22}H_{25}IN_2O_3$	53.67	5.12	25.77	5.69
XX	81	210–220[a]	45.53	4.01	36.87	5.02	$C_{21}H_{22}BrIN_2O_3$	45.27	3.98	37.11	5.03
XXI	90	230–240[a]	52.20	4.99	24.73	5.54	$C_{22}H_{25}IN_2O_4$	51.98	4.96	24.96	5.51

[a] With decomposition.

admission into the ion source (150°C). The purity of the products was checked by TLC on Silufol UV-254 plates using chloroform–ethyl acetate (2 : 1) and 2-propanol–water (4 : 1) as eluents and also by ^{1}H NMR spectroscopy and elemental analysis. Table 1 gives the ^{1}H NMR data for the compounds prepared, and their yields, melting points, and analytical data are listed in Table 2.

4-Methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinolin-5-ol (I, cotarnine). Cotarnine hydrochloride monohydrate (of pharmaceutical grade), 27.1 g (0.1 mol), was dissolved in 200 ml of water, a 10% aqueous solution of 0.105 mol of KOH was added with stirring, and the mixture was kept for 1 h at 15°C. The precipitate was filtered off, washed with water, and dried in a vacuum desiccator at 45°C. Yield 18.9 g (80%), mp 130–132°C; published data [10]: mp 133°C.

5-(1-Indolyl)-4-methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline (IV). Indole (**II**), 1.17 g (0.01 mol), was dissolved in 6 ml of methanol, 2.36 g (0.01 mol) of cotarnine (**I**) was added at 45°C, and the mixture was stirred until it became homogeneous and was left to stand at room temperature until a crystalline solid precipitated. The mixture was kept for 1 h at 15°C, and the precipitate was filtered off, washed with a small amount of cold methanol, and dried in a vacuum desiccator. Yield of product **IV** 3.17 g.

5-(5-Bromo-1-indolyl)-4-methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline (IX) was synthesized in a similar way from 5-bromoindole (**VI**) and compound **I**.

4-Methoxy-6-methyl-5-(2-methyl-1-indolyl)-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline (VIII). 2-Methylindole (**VII**), 1.31 g (0.01 mol), was dissolved in 7 ml of 85% methanol, 2.36 g (0.01 mol) of cotarnine (**I**) was added at 25°C, and the mixture was stirred until it became homogeneous and was left to stand for 24 h at room temperature. The precipitate was filtered off, washed with 50% methanol, and dried in a vacuum desiccator. Yield 1.65 g.

4-Methoxy-5-(5-methoxy-1-indolyl)-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline (X) was synthesized in a similar way from 5-methoxyindole (**IX**) and compound **I**.

5-(1-Indolyl)-4-methoxy-6,6-dimethyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinolinium iodide (V). Compound **IV**, 1.76 g (0.005 mol), was dissolved in 10 ml of chloroform at 40°C, and 2 ml of freshly distilled methyl iodide was added. The mixture was kept for 24 h at room temperature, and the precipitate was filtered off, washed with ether, and dried in a vacuum desiccator. Yield 2.35 g.

4-Methoxy-6,6-dimethyl-5-(2-methyl-1-indolyl)-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinolinium iodide (XI), 5-(5-bromo-1-indolyl)-4-methoxy-6,6-dimethyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinolinium iodide (XII), and 4-methoxy-5-(5-methoxy-1-indolyl)-6,6-dimethyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-*g*]isoquinolinium iodide (XIII) were synthesized in a similar way from compounds **VIII**–**X**, respectively.

5-(3-Indolyl)-4-methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline (XIV). A mixture of 1.76 g (0.005 mol) of compound **IV**, 15 ml of water, and 5 ml of alcohol was refluxed for 4 h under argon (to prevent exposure to air). The mixture was cooled to room temperature, and the precipitate was separated, washed with alcohol, and dried in a vacuum desiccator. Yield 1.26 g.

5-(2-Methyl-3-indolyl)-4-methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline (XV), 5-(5-bromo-3-indolyl)-4-methoxy-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline (XVI), and 4-methoxy-5-(5-methoxy-3-indolyl)-6-methyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinoline (XVII) were synthesized in a similar way from compounds **VIII**–**X**, respectively.

5-(3-Indolyl)-4-methoxy-6,6-dimethyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinolinium iodide (XVIII). Compound **XIV**, 1.76 g (0.005 mol), was dissolved in a minimal amount (30–40 ml) of chloroform at 40°C, the undissolved material was separated, and 2 ml of freshly distilled methyl iodide was added to the solution. The mixture was kept for 24 h at room temperature, and the precipitate was filtered off, washed with ether, and dried in a vacuum desiccator. Yield 2.2 g.

4-Methoxy-6,6-dimethyl-5-(2-methyl-3-indolyl)-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinolinium iodide (XIX), 5-(5-bromo-3-indolyl)-4-methoxy-6,6-dimethyl-5,6,7,8-tetrahydro[1,3]dioxolo[4,5-*g*]isoquinolinium iodide (XX), and 4-methoxy-5-(5-methoxy-3-indolyl)-6,6-dimethyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-*g*]isoquinolinium iodide (XXI) were synthesized in a similar way from compounds **XV**–**XVII**, respectively.

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