

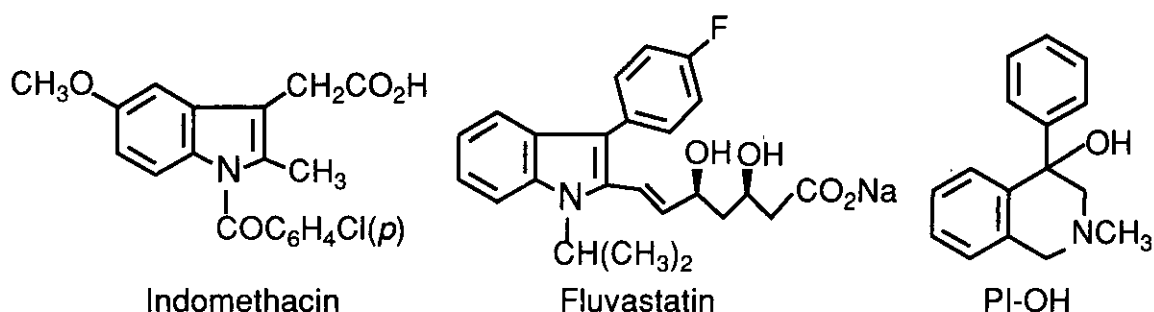
## A NEW SYNTHESIS OF 3-SUBSTITUTED INDOLINES AND INDOLES

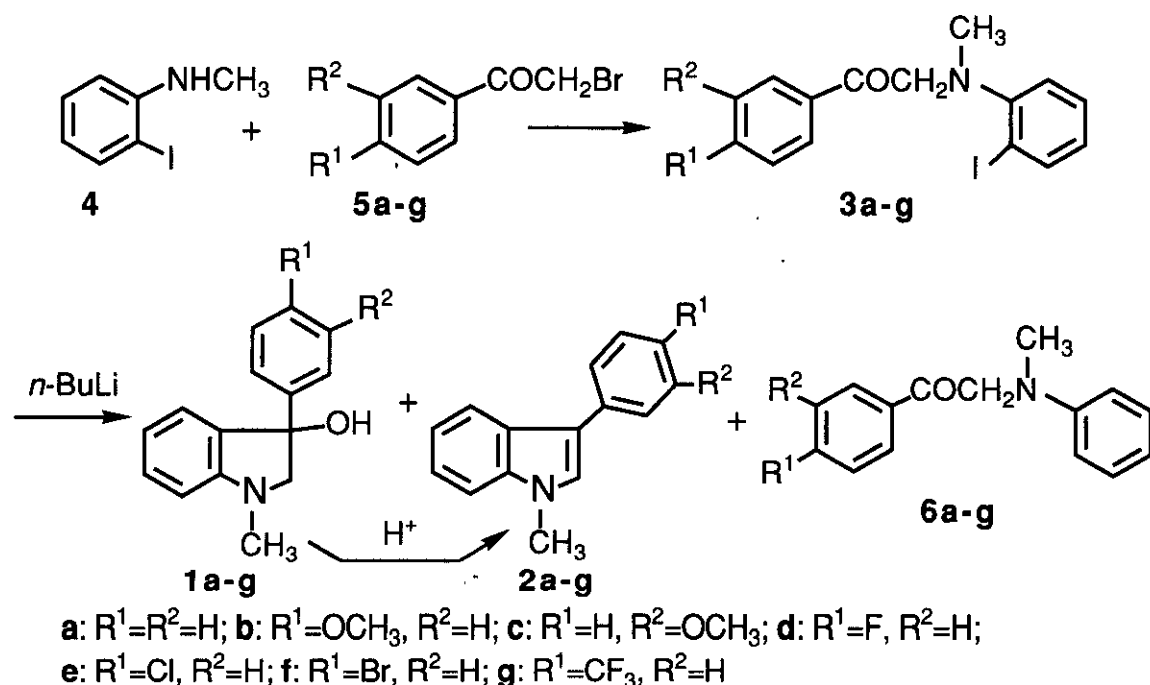
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**Abstract-** 3-Phenyl- and 3-alkyl-3-hydroxyindolines were synthesized by intramolecular Barbier reaction of phenyl and alkyl *N*-(2-iodophenyl)-*N*-methylaminomethyl ketones with *n*-BuLi, which were easily prepared from *N*-methyl-2-iodoaniline and bromomethyl ketones. The treatment of the indolines with acid gave the corresponding indoles in quantitative yields.

Many kinds of synthetic methods for 3-substituted indoles have been studied due to the significant biological and pharmacological activities of indole natural products<sup>1</sup> and of drugs such as indomethacin<sup>2</sup> and fluvastatin.<sup>3</sup> From these facts, we are interested in developing a new synthetic method for 3-substituted 3-hydroxyindolines since the 3-hydroxyindolines are expected to convert easily to the corresponding indoles. In addition, as 2-methyl-4-phenyl-1,2,3,4-tetrahydroisoquinolin-4-ol(PI-OH) and the related compounds showed a strong norepinephrine potentiating activity,<sup>4</sup> 3-phenyl-3-hydroxyindolines are also interesting compounds from a pharmacological point of view. We now report a new synthetic method for the preparation of 3-phenyl- and 3-alkyl-3-hydroxyindolines(1 and 7) and the corresponding indoles(2 and 8).





Scheme 1

In the previous papers,<sup>5</sup> we reported the synthesis of PI-OH and the related compounds by intramolecular Barbier reaction of *N*-benzylphenacylamines with *n*-BuLi. Thus, we planned the synthesis of 3-phenyl-3-hydroxyindolines (1) by intramolecular Barbier reaction of *N*-(2-iodophenyl)-*N*-methylphenacylamines (3) (Scheme 1). The synthesis of a key intermediate phenacylamine (3a) was attempted by the treatment of phenacyl bromide (5a) with 2-iodo-*N*-methylaniline (4) in the presence of propylene oxide (10 mol eq.) in various conditions as shown in Table I. The best result was obtained by using DMF as a solvent at 50°C (Entry 6). The reaction of other phenacyl bromides (5b-g) with 4 in

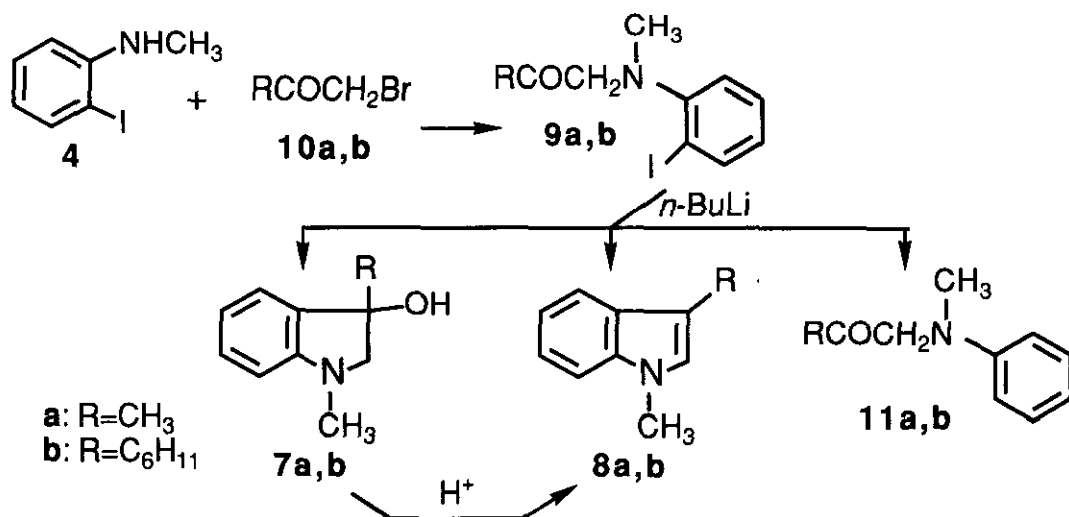
Table I. Synthesis of 3a from 4 and 5a

Entry	4 (mol eq.)	5a (mol eq.)	Propylene oxide (mol eq.)	Solvent	Temp. (°C)	Time (hr)	3a (%)
1	1.0	1.0	10	dioxane	reflux	100	30
2	1.0	1.0	10	DMSO	190	10min	---
3	1.0	1.0	10	DMSO	r.t. <sup>a)</sup>	96	58
4	1.0	1.0	10	DMF	r.t. <sup>a)</sup>	138	13
5	1.0	1.0	10	DMF	50	52	50
6	1.4	1.0	10	DMF	50	22	64

a) room temperature

the same conditions as Entry 6 gave phenacylamines(**3b-g**) in good yields, respectively. The phenacylamines(**3a-g**) were treated with *n*-BuLi in THF at  $-78^{\circ}\text{C}$  to give indolines(**1a-g**) along with indoles (**2a-g**) and deiodinated compounds (**6a-g**) as shown in Table II. Separation of the reaction mixture of **3d-g** with *n*-BuLi by flash chromatography gave the indolines(**1d-g**) and a small amount of the indoles(**2d-g**) as a pure compound, respectively. However, the chromatographic separation of the crude products<sup>6</sup> obtained by the reactions of **3a-c** with *n*-BuLi afforded a mixture of the indolines(**1a-c**) and the indoles(**2a-c**)(see Table II and Experimental). These facts suggest that the indolines(**1a-c**) have a higher tendency to dehydration and aromatization than the indolines(**1d-g**) possessing electron withdrawing substituents such as halogen atoms and a  $\text{CF}_3$  group on the 3-phenyl group. The indolines(**1d-g**) were converted by treatment with 5% HCl to the corresponding indoles(**2d-g**) in quantitative yields, respectively.

In the similar synthetic way, 3-hydroxy-3-alkylindolines(**7a,b**) and 3-alkylindoles (**8a,b**) were prepared as shown in Scheme 2. Methyl and cyclohexyl anilinomethyl ketones(**9a,b**) obtained from **4** and bromomethyl ketones(**10a,b**) were treated with *n*-BuLi, followed by chromatographic separation to give a mixture of the indolines(**7a,b**) and the indoles(**8a,b**) with the deiodinated products(**11a,b**) (Table II). Easy conversion of **1a-c** and **7a,b** to **2a-c** and **8a,b** was also ascertained by treatment of a chromatographically separated mixture of the corresponding indolines and indoles as shown in Table II with 5% HCl. These facts suggest that the treatment of the aminomethyl ketones such as **3a-g** and **9a,b** with *n*-BuLi, followed by dehydration of the crude product might provide a simple



Scheme 2

Table II. Yields of the indolines (**1a-g** and **7a,b**) and the indoles (**2a-g** and **8a,b**) from the ketones (**3a-g** and **9a,b**) with *n*-BuLi

Starting material	Yield (%) of Product					
	Indoline		Indole		By-product	
<b>3a</b> <sup>a)</sup>	<b>1a</b>	26	<b>2a</b>	53	<b>6a</b>	16
<b>3b</b> <sup>a)</sup>	<b>1b</b>	47	<b>2b</b>	24	<b>6b</b>	20
<b>3c</b> <sup>a)</sup>	<b>1c</b>	43	<b>2c</b>	23	<b>6c</b>	21
<b>3d</b>	<b>1d</b>	80	<b>2d</b>	4	<b>6d</b>	15
<b>3e</b>	<b>1e</b>	59	<b>2e</b>	4	<b>6e</b>	24
<b>3f</b>	<b>1f</b>	50	<b>2f</b>	3	<b>6f</b>	19
<b>3g</b>	<b>1g</b>	58	<b>2g</b>	2	<b>6g</b>	20
<b>9a</b> <sup>a)</sup>	<b>7a</b>	29	<b>8a</b>	48	<b>11a</b>	8
<b>9b</b> <sup>a)</sup>	<b>7b</b>	17	<b>8b</b>	62	<b>11b</b>	7

a) The reactions of **3a-c** and **9a,b** gave a mixture of the corresponding indolines and the indoles, respectively, after the chromatographic separation. The yields of the indolines and the indoles were determined by the <sup>1</sup>H-nmr spectra.

synthetic method of indoles(**2a-g** and **8a,b**). In fact, as a representative example, the cyclization of **3a** with *n*-BuLi and following dehydration of the crude product with 5% HCl gave **2a** in 77% yield with deiodinated product (**6a**)(13%).

In conclusion, an intramolecular Barbier reaction of phenyl and alkyl *N*-(2-iodophenyl)-*N*-methylaminomethy ketones with *n*-BuLi presented in this study provides a new and convenient method for the preparation of 3-substituted 3-hydroxyindolines and indoles.

## EXPERIMENTAL

All melting points are given as uncorrected values. High-resolution mass spectra were recorded on JELO SX-102A and JEOL JMS-D 300 spectrometers. <sup>1</sup>H-Nmr spectra were recorded on a JEOL JNM-FX 200 spectrometer in CDCl<sub>3</sub> with tetramethylsilane as a standard and are given in δ values.

***N*-Methyl-2-iodoaniline(4)** According to the method reported<sup>7</sup> by Kadin, a solution of *o*-iodoaniline(5.103 g, 23.3 mmol), succinimide(3.549 g, 34.0 mmol), and 37% formalin(2.8 ml, 34.5 mmol) in EtOH(30 ml) was refluxed for 24 h. The mixture was evaporated *in vacuo* and H<sub>2</sub>O(100 ml) was added to the residue. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>(100 ml x 3). The extract was washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and evaporated to give an oil(8.017 g). This was purified by flash chromatography on SiO<sub>2</sub> with CH<sub>2</sub>Cl<sub>2</sub>-acetone(30:1) to give *N*-(2-iodo-

anilinomethyl)succinimide as colorless prisms(6.129 g, 81%)(from CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane), mp 98-99°C. <sup>1</sup>H-Nmr(CDCl<sub>3</sub>) δ : 7.65(1H,dd, J=7.8, 1.5 Hz), 7.22(1H, ddd, J=7.3, 7.3, 1.5 Hz), 7.01(1H, dd, J=7.3, 1.5 Hz), 6.51(1H, ddd, J=7.8, 7.3, 1.5 Hz), 5.27(1H,t,J=7.8 Hz), 5.02 (2H,d,J=7.8 Hz), 2.67(4H,s). Ms(m/z)(M<sup>+</sup>): calcd for C<sub>11</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>: 329.9866. Found: 329.9844. Anal.Calcd for C<sub>11</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>: C, 40.02; H,3.36; N,8.49. Found: C, 40.04; H,3.41; N, 8.42.

NaBH<sub>4</sub>(689 mg, 16.4 mmol) was added to a solution of the *N*-(2-iodoanilino-methyl)succinimide(5.401 g, 16.4 mmol) obtained as above in dry DMSO(10 ml) and the mixture was heated for 30 min at 100°C. The reaction mixture was poured into ice-water(60 ml) and extracted with ether(60 ml x 3). The extract was dried over MgSO<sub>4</sub> and evaporated to give a pale brown oil. This was purified by flash chromatography on SiO<sub>2</sub> with *n*-hexane-CH<sub>2</sub>Cl<sub>2</sub>(1:1) to afford **4** as a pale yellow oil(3.463 g, 91%). <sup>1</sup>H-Nmr(CDCl<sub>3</sub>) δ :7.72(1H,dd,J=7.9, 1.5 Hz), 7.30(1H,ddd,J=8.8, 8.3, 1.5 Hz), 6.63(1H,dd,J=8.3, 1.5 Hz), 6.51(1H,ddd,J=8.8, 7.9, 1.5 Hz), 4.18(1H, br s), 2.95(3H,d,J=8.0 Hz). Ms(m/z) (M<sup>+</sup>): calcd for C<sub>7</sub>H<sub>8</sub>Nl: 232.9703. Found: 232.9703.

#### General Procedure for Preparation of Phenyl and Alkyl *N*-(2-Iodophenyl)-*N*-methylaminomethyl Ketones

This is exemplified by the preparation of **3d**. Propylene oxide(2.17 ml, 30.9 mmol) was added to a solution of 4-fluorophenacyl bromide(**5d**)(671 mg, 3.09 mmol) and *N*-methyl-2-iodoaniline (**4**)(1.004 g, 4.33 mmol) in dry DMF(2 ml). The mixture was heated under N<sub>2</sub> for 20 h at 50°C. H<sub>2</sub>O(20 ml) was added and the mixture was extracted with ether(20 ml x 3). The extract was evaporated and the residue was purified by flash chromatography on SiO<sub>2</sub> with *n*-hexane-CH<sub>2</sub>Cl<sub>2</sub>(1:1) as a eluent to give **3d** as an oil(881 mg, 86%). The ms and <sup>1</sup>H-nmr spectral data are shown in Table III.

Other *N*-(2-iodophenyl)-*N*-methylaminomethyl ketones(**3a-c**, **3e-g**, and **9a,b**) were prepared in the same way as **3d**(Table III).

#### General Procedure for Barbier Reaction of Phenyl and Alkyl *N*-(2-Iodophenyl)-*N*-methylaminomethyl Ketones

This is exemplified by the reaction of **3a** and **3d**. Reaction of **3a** *n*-BuLi(1.6 M sol. in *n*-hexane, 0.41 ml, 0.66 mmol) was added to a solution of the phenacylamine(**3a**)(195.5 mg, 0.55 mmol) in dry THF(5 ml) by a syringe at -78°C under N<sub>2</sub> and the mixture was stirred for 15 min at -78°C. H<sub>2</sub>O(10 ml) was added and the mixture was extracted with ether(20 ml x 3). The extract was dried over MgSO<sub>4</sub> and evaporated *in vacuo*. The residue was subjected to flash chromatography on SiO<sub>2</sub> with CH<sub>2</sub>Cl<sub>2</sub>. The first fraction was further purified by flash chromatography on SiO<sub>2</sub> with *n*-hexane-CH<sub>2</sub>Cl<sub>2</sub>(1:1) to afford the indole(**2a**) as an oil(17 mg) and the deiodinated product(**6a**) as a white solid(19.6 mg, 16%). The second fraction gave a mixture(75 mg) of **1a** and **2a** as an oil. The yields of **1a** and **2a** were calculated by the integral values of the *N*-

Table III. Yields, Ms and <sup>1</sup>H-Nmr Spectral Data for Aminomethyl Ketones(**3a-g** and **9a,b**)

No	Yield (%)	Formula	Ms(m/z)(M <sup>+</sup> ) Calcd(Found)	<sup>1</sup> H-Nmr (CDCl <sub>3</sub> ) δ
<b>3a</b>	64	C <sub>15</sub> H <sub>14</sub> NOI	351.0120 (351.0101)	7.97(2H,dd,J=8.3, 1.2 Hz), 7.83(1H,dd,J=8.1, 1.2 Hz), 4.52(2H,s), 2.95(3H,s)
<b>3b</b>	61	C <sub>16</sub> H <sub>16</sub> NO <sub>2</sub> I	381.0228 (381.0214)	8.00(2H,d,J=9.0 Hz), 7.82(1H,dd,J=7.9, 1.2 Hz), 6.89(2H,d,J=9.0 Hz), 4.45(2H,s), 3.86(3H,s), 2.92(3H,s)
<b>3c</b>	86	C <sub>16</sub> H <sub>16</sub> NO <sub>2</sub> I	381.0228 (381.0263)	7.82(1H,dd,J=7.9, 1.3 Hz), 7.54(1H,ddd,J=7.8, 1.5, 1.0 Hz), 7.48(1H,dd,J=2.7, 1.5 Hz), 7.34(1H,dd,J=8.3, 7.8 Hz), 7.10(1H,ddd,J=8.3, 2.7, 1.0 Hz), 4.52(2H,s), 3.84(3H,s), 2.95(3H,s)
<b>3d</b>	86	C <sub>15</sub> H <sub>13</sub> NOFI	369.0026 (369.0054)	8.05(2H,dd,J=8.5, 5.5 Hz), 7.83(1H,dd,J=7.8, 1.5 Hz), 7.11(2H,dd,J=8.5, 8.5 Hz), 6.80(1H,m), 4.46(3H,s), 2.91(3H,s)
<b>3e</b>	61	C <sub>15</sub> H <sub>13</sub> NOClI	384.9730 (384.9765)	7.94(2H,d,J=8.7 Hz), 7.82(1H,dd,J=7.8, 1.5 Hz), 7.41(2H,d,J=8.7 Hz), 7.32(1H,ddd,J=8.1, 7.8, 1.5 Hz), 6.79(1H,ddd,J=8.1, 7.8, 2.0 Hz), 4.45(2H,s), 2.91(3H,s)
<b>3f</b>	82	C <sub>15</sub> H <sub>13</sub> NOBrI	428.9225 (428.9254)	7.86(2H,d,J=8.4 Hz), 7.83(1H,dd,J=8.3, 1.5 Hz), 7.58(2H,d,J=8.4 Hz), 4.44(2H,s), 2.90(3H,s)
<b>3g</b>	38	C <sub>16</sub> H <sub>13</sub> NOF <sub>3</sub> I	418.9994 (418.9985)	8.09(2H,d,J=8.1 Hz), 7.83(1H,dd,J=8.0, 1.5 Hz), 7.71(2H,d,J=8.1 Hz), 6.80(1H,ddd,J=7.5, 6.8, 2.0 Hz), 4.50(2H,s), 2.92(3H,s)
<b>9a</b>	91	C <sub>10</sub> H <sub>12</sub> NOI	288.9964 (288.9976)	7.85(1H,dd,J=7.8, 1.5 Hz), 7.13(1H,dd,J=8.1, 1.5 Hz), 6.80(1H,ddd,J=8.1, 7.3, 1.5 Hz), 3.78(2H,s), 2.80(3H,s), 2.23(3H,s)
<b>9b</b>	58	C <sub>15</sub> H <sub>20</sub> NOI	357.0590 (357.0586)	7.86(1H,dd,J=7.8, 1.5 Hz), 7.14(1H,dd,J=8.1, 1.5 Hz), 6.78(1H,ddd,J=8.8, 7.1, 1.5 Hz), 3.86(2H,s), 2.79(3H,s), 2.63(1H,m)

methyl groups in the <sup>1</sup>H-nmr spectrum to be 32 mg(26%) and 43 mg(total yield 60 mg, 53%). The ms and <sup>1</sup>H-nmr spectral data are shown in Table IV.

Intramolecular Barbier reaction of other ketones(**3b,c** and **9a,b**) were carried out in the same way as **3a**(Tables II, IV, and V).

**Reaction of 3d** The phenacylamine(**3d**)(739 mg, 2.0 mmol) was treated with *n*-BuLi (1.6 M sol. in hexane, 1.56 ml, 2.40 mmol) in dry THF(10 ml) in the same way as **3a** to give a crude product(566.8 mg). This was subjected to flash chromatography on SiO<sub>2</sub> with CH<sub>2</sub>Cl<sub>2</sub> to give **2d**(first fraction: 18 mg, 4%), **6d**(second fraction: 54 mg, 15%), and **1d**(third fraction: 389 mg, 80%), respectively. The ms and <sup>1</sup>H-nmr spectral data of these products are shown in Table IV.

Other phenacylamines(**3e-g**) were treated in the same way as **3d**(Tables II and IV).

**General Procedure for Dehydration of 3-Phenyl- and 3-Alkyl-3-hydroxy-1-methylindolines** This is exemplified by dehydration of **1d** with 5% HCl. 5% HCl(5 ml) was added to a solution of **1d**(46.2 mg, 0.19 mmol) in ether(5 ml) and the mixture was stirred for 10 min at room temperature. The mixture was made basic with 10% KOH and extracted with CH<sub>2</sub>Cl<sub>2</sub>(20 ml x 3).

Table IV. Ms and <sup>1</sup>H-Nmr Spectral Data for the Indolines(1a-g), Indoles(2a-g), and Deiodinated Products(6a-g)

No	Formula	Ms(m/z)(M <sup>+</sup> ) Calcd(Found)	<sup>1</sup> H-Nmr (CDCl <sub>3</sub> ) δ
1 a	C <sub>15</sub> H <sub>15</sub> NO	225.1154 (225.1138)	7.53(2H,d,J=8.5 Hz), 6.98(1H,d,J=7.7 Hz), 6.65(1H,d,J=8.5 Hz), 3.63, 3.41(each 1H, d,J=10.3 Hz),2.85(3H,s)
1 b	C <sub>16</sub> H <sub>17</sub> NO <sub>2</sub>	255.1260 (255.1272)	7.44, 6.87(each 2H,d,J=8.4 Hz), 6.64(1H,d,J=7.8 Hz), 3.79(3H, s), 3.60, 3.37(each 1H,d,J=10.3 Hz), 2.83(3H,s)
1 c	C <sub>16</sub> H <sub>17</sub> NO <sub>2</sub>	255.1260 (255.1286)	6.73(1H,ddd,J=7.3, 7.3, 1.0 Hz), 6.64(1H,d,J=8.1 Hz), 3.63, 3.41(each 1H, d,J=10.3 Hz), 3.80(3H,s), 2.88(3H,s)
1 d	C <sub>15</sub> H <sub>14</sub> NOF	243.1059 (243.1057)	7.49(2H,dd,J=9.0, 5.4 Hz), 7.01(2H,dd,J=9.0, 9.0 Hz), 6.65(1H, d,J=8.1 Hz), 3.60, 3.37(each 1H,d,J=10.3 Hz), 2.84(3H,s)
1 e	C <sub>15</sub> H <sub>14</sub> NOCl	259.0764 (259.0745)	7.46, 7.30(each 2H,d,J=8.8 Hz), 6.95(1H,dd,J=7.3, 1.0 Hz), 6.64 (1H,d,J=7.8 Hz), 3.60, 3.37(each 1H,d,J=10.3 Hz), 2.84(3H,s)
1 f	C <sub>15</sub> H <sub>14</sub> NOBr	303.0259 (303.0258)	7.45, 7.41(each 2H,d,J=9.0 Hz), 6.95(1H,dd,J=8.3, 1.5 Hz), 6.65 (1H,d,J=8.1 Hz), 3.61, 3.37(each 1H,d,J=10.5 Hz), 2.84(3H,s)
1 g	C <sub>16</sub> H <sub>14</sub> NOF <sub>3</sub>	293.1028 (293.0994)	7.67, 7.59(each 2H,d,J=8.6 Hz), 6.95(1H,dd,J=7.3, 1.2 Hz), 6.67 (1H,d,J=8.3 Hz), 3.64, 3.43(each 1H,d,J=10.7 Hz), 2.87(3H,s)
2 a	C <sub>15</sub> H <sub>13</sub> N	207.1048 (207.1040)	7.94(1H,dd,J=7.6, 1.5 Hz), 7.66(2H,dd,J=8.3, 1.2 Hz), 7.20 (1H,s), 3.80(3H,s)
2 b	C <sub>16</sub> H <sub>15</sub> NO	237.1154 (237.1153)	7.89(1H,d,J=8.1 Hz), 7.65, 7.06(each 2H,d,J=8.8 Hz), 7.36(1H, d,J=7.8 Hz), 7.16(1H,s), 3.86(3H,s), 3.83(3H,s)
2 c	C <sub>16</sub> H <sub>15</sub> N	237.1154 (237.1147)	7.95(1H,dd,J=8.1, 1.2 Hz), 7.24(1H,s), 6.82(1H,ddd,J=8.1, 2.7, 1.2 Hz), 3.87(3H,s), 3.84(3H,s)
2 d	C <sub>15</sub> H <sub>12</sub> NF	225.0954 (225.0948)	7.86(1H,dd,J=7.1, 1.2 Hz), 7.58(2H,dd,J=8.8, 5.4 Hz), 7.16(1H, s), 7.12(2H,dd,J=8.8, 8.8 Hz), 3.81(3H,s)
2 e	C <sub>15</sub> H <sub>12</sub> NCl	241.0658 (241.0650)	7.88(1H,dd,J=8.6, 1.0 Hz), 7.58, 7.39(each 2H,d,J=8.4 Hz), 7.22(1H,s), 3.85(3H,s)
2 f	C <sub>15</sub> H <sub>12</sub> NBr	285.0153 (285.0171)	7.88(1H,d,J=7.3 Hz, 7.52(4H,s), 7.22(1H,s), 3.83(3H,s)
2 g	C <sub>16</sub> H <sub>12</sub> NF <sub>3</sub>	275.0922 (275.0930)	7.91(1H,d,J=8.1 Hz), 7.72, 7.64(each 2H,d,J=8.3 Hz), 7.25 (1H,s), 3.79(3H,s)
6 a	C <sub>15</sub> H <sub>15</sub> NO	225.1154 (225.1161)	7.99(2H,dd,J=8.1, 1.5 Hz), 7.21(2H,dd,J=8.8, 7.3 Hz), 6.72(1H, t,J=7.3 Hz), 6.68(2H,d,J=7.8 Hz), 4.77(2H,s), 3.10(3H,s)
6 b	C <sub>16</sub> H <sub>17</sub> NO <sub>2</sub>	255.1259 (255.1247)	7.97, 6.96(each 2H,d,J=9.0 Hz), 7.20(2H,dd,J=8.8, 7.3 Hz), 6.71 (1H,t,J=7.3 Hz), 4.72(2H,s), 3.88(3H,s), 3.09(3H,s)
6 c	C <sub>16</sub> H <sub>17</sub> NO <sub>2</sub>	225.1259 (255.1236)	7.57(1H,ddd, J=7.8, 1.5, 1.2 Hz), 7.50(1H,dd,J=2.7, 1.5 Hz), 6.67(2H,dd,J=8.8, 1.0 Hz), 4.76(2H,s), 3.84(3H,s), 3.10(3H,s)
6 d	C <sub>15</sub> H <sub>14</sub> NOF	243.1059 (243.1059)	8.01(2H,dd,J=8.8, 5.4 Hz), 7.15(2H,dd,J=8.6, 8.6 Hz), 6.73(1H, t,J=7.1 Hz), 6.67(2H,d,J=8.3 Hz), 4.72(2H,s), 3.09(3H,s)
6 e	C <sub>15</sub> H <sub>14</sub> NOCl	259.0764 (259.0774)	7.92, 7.46(each 2H,d,J=8.8 Hz), 7.21(2H,dd,J=8.8, 7.3 Hz), 6.74 (1H,t,J=7.3 Hz),6.67(1H,dd,J=8.8, 1.2 Hz),4.72(2H,s),3.09(3H,s)
6 f	C <sub>15</sub> H <sub>14</sub> NOBr	303.0259 (303.0302)	7.85, 7.63(each 2H,d,J=8.8 Hz), 7.21(2H,dd,J=8.5, 7.1 Hz), 6.74 (1H,t,J=7.1 Hz),6.67(2H,dd,J=8.5, 1.2 Hz),4.72(2H,s),3.09(3H,s)
6 g	C <sub>16</sub> H <sub>14</sub> NOF <sub>3</sub>	293.1027 (293.1005)	8.08,7.76(each 2H,d,J=8.2 Hz),7.22(2H,ddd,J=8.3, 7.1, 1.2 Hz), 6.75(1H,t,J=7.1 Hz), 6.68(2H,d,J=8.3 Hz), 4.77(2H,s),3.10(3H,s)

Table V. Ms and <sup>1</sup>H-Nmr Spectral Data for the Indolines(7a,b), Indoles( 8a,b) and Deiodinated Products(11a,b)

No	Formula	Ms(m/z)(M <sup>+</sup> ) Calcd(Found)	<sup>1</sup> H-Nmr (CDCl <sub>3</sub> ) δ
7a	C <sub>10</sub> H <sub>13</sub> NO	163.0997 (163.1000)	6.75(1H,dd,J=7.6, 7.6 Hz), 6.54(1H,d,J=7.8 Hz), 3.37, 3.16 (each 1H,d,J=10.0 Hz), 2.78(3H,s), 1.62(3H,s)
7b	C <sub>15</sub> H <sub>21</sub> NO	231.1623 (231.1599)	6.72(1H,ddd,J=7.6, 7.6, 1.0 Hz), 6.53(1H,dd,J=8.5, 1.0 Hz), 3.40, 3.16(each 1H,d,J=10.3 Hz), 2.78(3H,s), 2.80(1H,m)
8a	C <sub>10</sub> H <sub>11</sub> N	145.0892 (145.0890)	7.56(1H,dd,J=6.8, 1.2 Hz), 6.79(1H,s), 3.69(3H,s), 2.31(3H,s)
8b	C <sub>15</sub> H <sub>19</sub> N	213.1517 (213.1532)	7.63(1H,dd,J=7.7, 1.0 Hz), 7.20(1H,dd,J=8.3, 1.2 Hz), 7.06(1H,ddd,J=8.1, 7.8, 1.5 Hz), 6.76(1H,s), 3.68(3H,s), 2.85(1H,m)
11a	C <sub>10</sub> H <sub>13</sub> NO	163.0997 (163.1010)	7.23(2H,dd,J=8.8, 7.3 Hz), 6.75(1H,t,J=7.3 Hz), 6.62(2H,dd,J=8.8, 0.9 Hz), 4.01(2H,s), 3.06(3H,s), 2.13(3H,s)
11b	C <sub>15</sub> H <sub>21</sub> NO	231.1623 (231.1617)	7.21(2H,dd,J=7.6, 7.1 Hz), 6.72(1H,t,J=7.6 Hz), 6.60(2H,d,J=7.1 Hz), 4.01(2H,s), 3.02(3H,s), 2.50(1H,m)

The extract was washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and evaporated *in vacuo* to give **2d** as an oil(42 mg, 98%).

Other indolines(**1e-g**) were dehydrated in the same way as **1d**.

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6. The crude products were found to contain the indolines **1a-c** as a major product with a trace of the indoles(**2a-c**) by their  $^1\text{H}$ -nmr spectra, respectively.
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