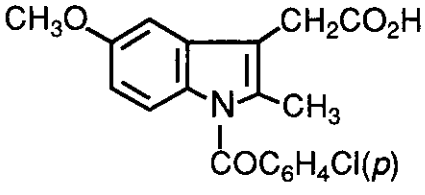
A NEW SYNTHESIS OF 3-SUBSTITUTED INDOLINES AND INDOLES

Masaru Kihara,* Yasumasa Iwai, and Yoshimitsu Nagao

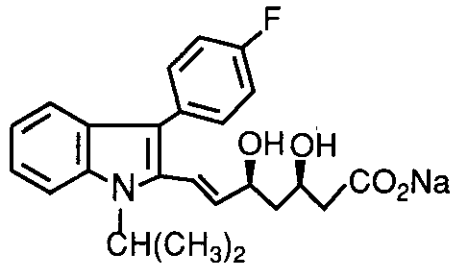
Faculty of Pharmaceutical Sciences, The University of Tokushima, Sho-machi, Tokushima 770, Japan

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.

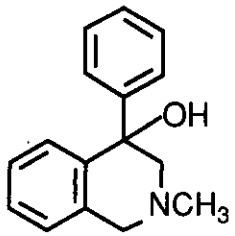
Many kinds of synthetic methods for 3-substituted indoles have been studied due to the significant biological and pharmacological actitivities of indole natural products[1] and of drugs such as indomethacin[2] and fluvastatin.[3] From these facts, we are interested in developing a new synthetic method 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,[4] 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**).



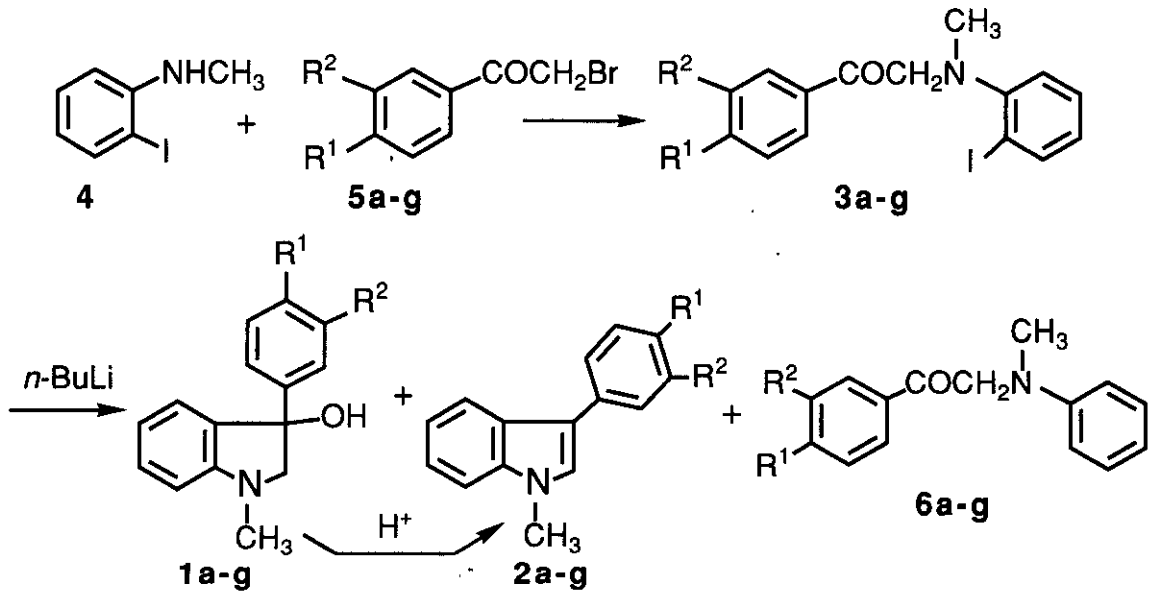
Indomethacin



Fluvastatin



PI-OH



a: R^1=R^2=H; **b**: R^1=OCH_3, R^2=H; **c**: R^1=H, R^2=OCH_3; **d**: R^1=F, R^2=H;
e: R^1=Cl, R^2=H; **f**: R^1=Br, R^2=H; **g**: R^1=CF_3, R^2=H

Scheme 1

In the previous papers,[5] 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 propyrene 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

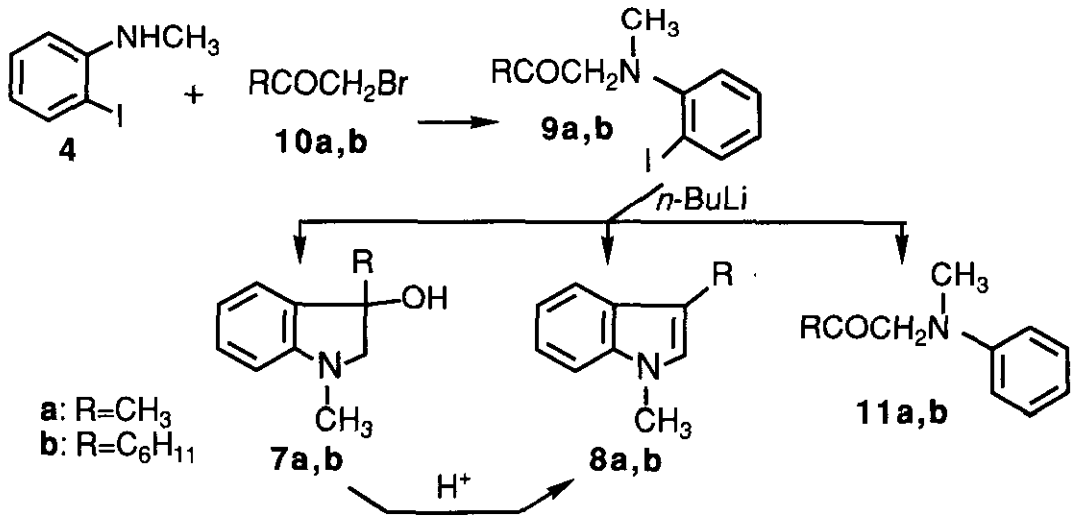
Table I. Synthesis of **3a** from **4** and **5a**

Entry	**4** (mol eq.)	**5a** (mol eq.)	Propyrene 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.[a)]	96	58
4	1.0	1.0	10	DMF	r.t.[a)]	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°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[6] 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 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	
3a [a]	**1a**	26	**2a**	53	**6a**	16
3b [a]	**1b**	47	**2b**	24	**6b**	20
3c [a]	**1c**	43	**2c**	23	**6c**	21
3d	**1d**	80	**2d**	4	**6d**	15
3e	**1e**	59	**2e**	4	**6e**	24
3f	**1f**	50	**2f**	3	**6f**	19
3g	**1g**	58	**2g**	2	**6g**	20
9a [a]	**7a**	29	**8a**	48	**11a**	8
9b [a]	**7b**	17	**8b**	62	**11b**	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 ^{1}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. ^{1}H-Nmr spectra were recorded on a JEOL JNM-FX 200 spectrometer in $CDCl_3$ with tetramethylsilane as a standard and are given in δ values.

***N*-Methyl-2-iodoaniline(4)** According to the method reported[7] 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_2O(100 ml) was added to the residue. The mixture was extracted with CH_2Cl_2(100 ml x 3). The extract was washed with H_2O, dried over $MgSO_4$, and evaporated to give an oil(8.017 g). This was purified by flash chromatography on SiO_2 with CH_2Cl_2-acetone(30:1) to give *N*-(2-iodo-

anilinomethy)succinimide as colorless prisms(6.129 g, 81%)(from CH_2Cl_2-*n*-hexane), mp 98-99°C. ^{1}H-Nmr($CDCl_3$) 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^+): calcd for $C_{11}H_{11}N_2IO_2$: 329.9866. Found: 329.9844. Anal.Calcd for $C_{11}H_{11}N_2IO_2$: C, 40.02; H,3.36; N,8.49. Found: C, 40.04; H,3.41; N, 8.42.

$NaBH_4$(689 mg, 16.4 mmol) was added to a solution of the *N*-(2-iodoanilinomethy)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 $MgSO_4$ and evaporated to give a pale brown oil. This was purified by flash chromatography on SiO_2 with *n*-hexane-CH_2Cl_2(1:1) to afford **4** as a pale yellow oil(3.463 g, 91%). ^{1}H-Nmr($CDCl_3$) 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^+): calcd for C_7H_8NI: 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**. Propyrene 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_2 for 20 h at 50°C. H_2O(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_2 with *n*-hexane-CH_2Cl_2(1:1) as a eluent to give **3d** as an oil(881 mg, 86%). The ms and ^{1}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_2 and the mixture was stirred for 15 min at -78°C. H_2O(10 ml) was added and the mixture was extracted with ether(20 ml x 3). The extract was dried over $MgSO_4$ and evaporated *in vacuo*. The residue was subjected to flash chromatography on SiO_2 with CH_2Cl_2. The first fraction was further purified by flash chromatography on SiO_2 with *n*-hexane-CH_2Cl_2(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 ^{1}H-Nmr Spectral Data for Aminomethyl Ketones(**3a-g** and **9a,b**)

No	Yield (%)	Formula	Ms(m/z)(M$^+$) Calcd(Found)	^{1}H-Nmr ($CDCl_3$) δ
3a	64	$C_{15}H_{14}NOI$	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)
3b	61	$C_{16}H_{16}NO_2I$	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)
3c	86	$C_{16}H_{16}NO_2I$	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)
3d	86	$C_{15}H_{13}NOFI$	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)
3e	61	$C_{15}H_{13}NOClI$	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)
3f	82	$C_{15}H_{13}NOBrI$	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)
3g	38	$C_{16}H_{13}NOF_3I$	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)
9a	91	$C_{10}H_{12}NOI$	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)
9b	58	$C_{15}H_{20}NOI$	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 ^{1}H-nmr spectrum to be 32 mg(26%) and 43 mg(total yield 60 mg, 53%). The ms and ^{1}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_2 with CH_2Cl_2 to give **2d**(first fraction: 18 mg, 4%), **6d** (second fraction: 54 mg, 15%), and **1d**(third fraciton: 389 mg, 80%), respectively. The ms and ^{1}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_2Cl_2(20 ml x 3).

Table IV. Ms and ^{1}H-Nmr Spectral Data for the Indolines(**1a-g**) , Indoles(**2a-g**), and Deiodinated Products(**6a-g**)

No	Formula	Ms(m/z)(M$^+$) Calcd(Found)	^{1}H-Nmr ($CDCl_3$) δ
1a	$C_{15}H_{15}NO$	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)
1b	$C_{16}H_{17}NO_2$	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)
1c	$C_{16}H_{17}NO_2$	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)
1d	$C_{15}H_{14}NOF$	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)
1e	$C_{15}H_{14}NOCl$	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)
1f	$C_{15}H_{14}NOBr$	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)
1g	$C_{16}H_{14}NOF_3$	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)
2a	$C_{15}H_{13}N$	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)
2b	$C_{16}H_{15}NO$	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)
2c	$C_{16}H_{15}N$	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)
2d	$C_{15}H_{12}NF$	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)
2e	$C_{15}H_{12}NCl$	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)
2f	$C_{15}H_{12}NBr$	285.0153 (285.0171)	7.88(1H,d,J=7.3 Hz, 7.52(4H,s), 7.22(1H,s), 3.83(3H,s)
2g	$C_{16}H_{12}NF_3$	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)
6a	$C_{15}H_{15}NO$	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)
6b	$C_{16}H_{17}NO_2$	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)
6c	$C_{16}H_{17}NO_2$	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)
6d	$C_{15}H_{14}NOF$	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)
6e	$C_{15}H_{14}NOCl$	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)
6f	$C_{15}H_{14}NOBr$	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)
6g	$C_{16}H_{14}NOF_3$	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 ^{1}H-Nmr Spectral Data for the Indolines(**7a**,**b**), Indoles(**8a**,**b**) and Deiodinated Products(**11a**,**b**)

No	Formula	Ms(m/z)(M$^+$) Calcd(Found)	^{1}H-Nmr ($CDCl_3$) δ
7a	$C_{10}H_{13}NO$	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	$C_{15}H_{21}NO$	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	$C_{10}H_{11}N$	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	$C_{15}H_{19}N$	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	$C_{10}H_{13}NO$	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	$C_{15}H_{21}NO$	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_2O, dried over $MgSO_4$, 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}H-nmr spectra, respectively.
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