Photocyclisation of Enamides. Part 20.[1] Photocyclisation of *N*-Naphthylacrylamides and Synthesis of the Basic Indolo[4,3-*fg*]quinoline Nucleus of Ergot Alkaloids[2]

Ichiya Ninomiya,* Chiyomi Hashimoto, Toshiko Kiguchi, and Takeaki Naito
Kobe Women's College of Pharmacy, Motoyamakita, Higashinada, Kobe 658, Japan

Photocyclisation of some *N*-naphthylacrylamides (1)—(6) provided a general synthetic route to benzo[*h*]- and benzo[*f*]-quinolines (7)—(12) and two compounds containing the basic indolo[4,3-*fg*]quinoline nucleus of ergot alkaloids, (17) and (21), were readily prepared.

Though non-oxidative photocyclisation of simple α,β-unsaturated acylanilides was reported first by Chapman[3] and Ogata,[4] and then by our group,[5] the photochemistry of *N*-naphthylacrylamides remains unexplored to date.

As an extension of our work on enamide photocyclisations,[5b] we now report the non-oxidative photocyclisation of *N*-(1- and 2-naphthyl)acrylamides and also the application of the photocyclisation to the synthesis of the basic indolo-[4,3-*fg*]quinoline nucleus of ergot alkaloids. In addition to the conventional methods[6] for the preparation of benzo[*h*]- and benzo[*f*]-quinolines, the photochemical synthesis described here would provide a new and simple methodology with a wide applicability to the synthesis of some heterocyclic compounds related to ergot alkaloids.

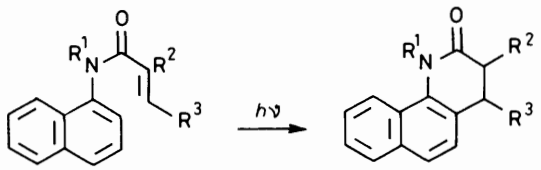
Preparation and Photocyclisation of N-*Naphthylacrylamides* (1)—(6).—All the *N*-naphthylacrylamides (1)—(6) were readily prepared by acylation of the corresponding 1- and 2-naphthylamine with acryloyl chloride and its substituted congeners in good yield except the methacrylamide (6d) which was prepared by methylation of (6c).

The structures of all the *N*-naphthylacrylamides (1)—(6) were readily established from their i.r. spectra [$\nu_{max.}$ 1 695—1 620 cm^{-1} (NCO)] and also from their n.m.r. spectra which exhibited signals showing the presence of olefinic protons.

A 0.02—0.005M solution of each *N*-naphthylacrylamide in a solvent such as methanol, benzene, or acetic acid was irradiated with a low-pressure mercury lamp at room temperature as described previously.[7] The *N*-(1-naphthyl)acrylamides (1a), (2a), and (3a) underwent smooth photocyclisation to afford the corresponding benzo[*h*]quinolones (7a), (8a), and (9a) in comparatively good yield.

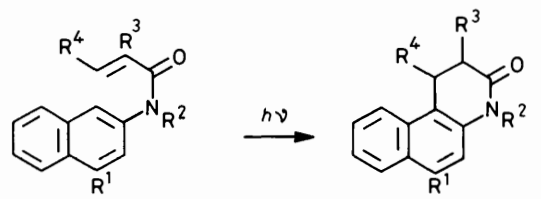
On the other hand, in the case of the *N*-methylacrylamides (1b), (2b), and (3b) the occurrence of the photocyclisation depended on the substituents on the acryloyl group as follows; the methacrylamide (3b) afforded the photocyclised lactam (9b) while the acrylamide (1b) and the cinnamamide (2b) were recovered unchanged upon irradiation under various conditions. The substituent effect on the photocyclisations described in this paper seems to be very similar to those reported previously for the photocyclisation of acrylanilides.[3,4]

On the other hand, photocyclisation of all the *N*-(2-naphthyl)acrylamides (4a and b), (5), and (6a—d) proceeded very smoothly irrespective of the substituents on the nitrogen and the acryloyl group to afford the corresponding benzo[*f*]quinolones (10a and b) (11), and (12a—d) in good yield. The exclusive formation of benzo[*f*]quinolones by photocyclisation of the *N*-(2-naphthyl)acrylamides and the better yield than that obtained from photocyclisation of the *N*-(1-naphthyl)-acrylamides can be ascribed to the different reactivities of the 1- and 2-position on the naphthalene ring in the respective naphthylacrylamides. During the course of irradiation of the *N*-naphthylacrylamides (1)—(6), none of the acyl-migrated



(1a and b) (7a)
(2a and b) (8a)
(3a and b) (9a and b)

(1a) (7a) $R^1 = R^2 = R^3 = H$
(1b) $R^1 = Me, R^2 = R^3 = H$
(2a) (8a) $R^1 = R^2 = H, R^3 = Ph$
(2b) $R^1 = Me, R^2 = H, R^3 = Ph$
(3a) (9a) $R^1 = R^3 = H, R^2 = Me$
(3b) (9b) $R^1 = R^2 = Me, R^3 = H$

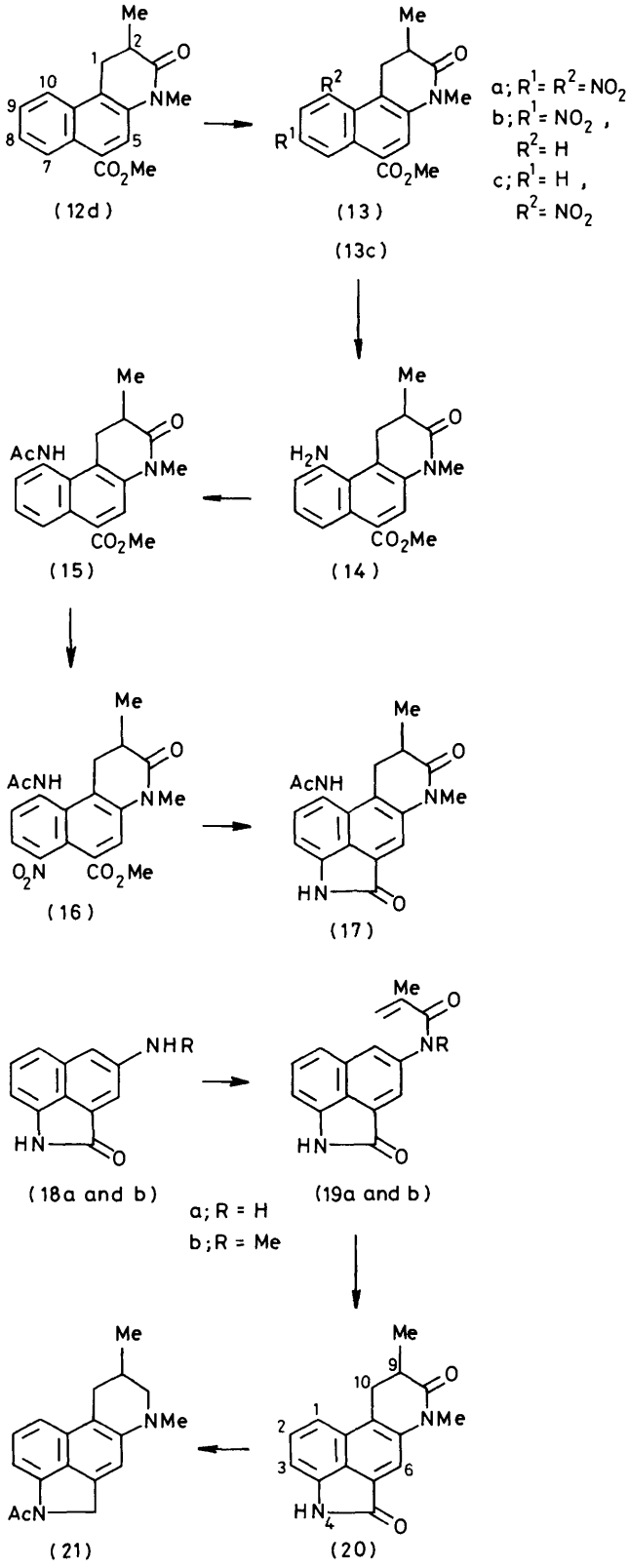


(4a and b) (10a and b)
(5) (11)
(6a—d) (12a—d)

(4a) (10a) $R^1 = R^2 = R^3 = R^4 = H$
(4b) (10b) $R^1 = R^3 = R^4 = H, R^2 = Me$
(5) (11) $R^1 = R^3 = H, R^2 = Me, R^4 = Ph$
(6a) (12a) $R^1 = R^2 = R^4 = H, R^3 = Me$
(6b) (12b) $R^1 = R^4 = H, R^2 = R^3 = Me$
(6c) (12c) $R^1 = CO_2Me, R^2 = R^4 = H, R^3 = Me$
(6d) (12d) $R^1 = CO_2Me, R^2 = R^3 = Me, R^4 = H$

products was detected.[8] It was also observed that the presence of small amounts of acetic acid in the irradiation solution considerably increased the yield of photocyclisation products.

Synthesis of Derivatives of Indolo[4,3-fg]*quinoline, the Basic Skeletal Nucleus of Ergot Alkaloids.*—Starting from the benzo[*f*]quinolone (12d) which carries an ester group at the 6-position, the synthesis of the basic indolo[4,3-*fg*]quinoline nucleus of ergot alkaloids was investigated as follows. Since the introduction of a nitro group at the 7-position *peri* to a carboxy group of benzo[*f*]quinoline skeletons had been reported,[9] we attempted the nitration of the photocyclised product (12d). However, the nitro group was introduced not at the desired



7-position but at both the 8- and 10-positions giving a mixture of three nitrated products (13a—c). Therefore, in order to prepare the compound having the skeletal nucleus of ergot alkaloids, the 10-mono-nitro derivative (13c) was employed for further transformation. Thus, reduction of (13c) with Raney-nickel and hydrazine yielded the 10-aminobenzo[*f*]-quinolone (14) which was then acetylated. Again, nitration of the acetylated derivative (15) afforded the mono-nitro product (16) which was then transformed by reduction with Raney-nickel and hydrazine into the corresponding indolo-[4,3-*fg*]quinoline-5,8-dione (17), which unambiguously established the position of the second nitro group as shown. However, the above result, which did not seem very promising as a preparative method for ergot alkaloids though their basic nucleus had been synthesized, led us to investigate further the photocyclisation of the *N*-methacrylamides (19a and b). Since irradiation of the *N*-(benz[*cd*]indol-4-yl)methacrylamide (19a) prepared from the 4-aminobenzindolone (18a) [10] unexpectedly brought about no cyclisation but gave only a full recovery of the starting material, we then investigated the photocyclisation of the corresponding *N*-methylmethacrylamide (19b), which was prepared as follows. 4-Methylamino-1,2-dihydrobenz[*cd*]indol-2-one (18b) was synthesized *via* the Schiff's base of compound (18a), followed by reduction, methylation, and debenzylation, in 44% overall yield though attempted preparation of (18b) by the method described in the literature [10] was unsuccessful.

Acylation of compound (18b) with methacryloyl chloride yielded the corresponding *N*-methylmethacrylamide (19b) in good yield. Photocyclisation of the *N*-methylmethacrylamide (19b) in benzene–acetic acid (15 : 1) solution proceeded smoothly to afford the lactam (20) in 42% yield. Reduction of the lactam (20) with lithium aluminium hydride gave the corresponding amine, which was characterised as its acetate (21), in 50% yield.

Experimental

^1H N.m.r. spectra were measured with Varian A-60D and JEOL PMX-60 instruments for solutions in deuteriochloroform unless otherwise stated (tetramethylsilane as internal reference), mass spectra with a JEOL JMS-O1SG machine, and i.r. spectra for solutions in chloroform on a Hitachi 215 spectrophotometer. M.p.s were determined with a Kofler-type hot-stage apparatus. The extracts from the reaction mixture were dried over anhydrous sodium sulphate. The photochemical reactions were carried out by irradiation with a low-pressure (120 W) mercury lamp (Eikosha, Osaka, Japan, PIL 120) at room temperature.

General Procedure for the Preparation of N-*Naphthylacrylamides* (1)—(6).—To a stirred solution of the respective naphthylamine (0.1 mol) or *N*-methylnaphthylamine (0.1 mol) and triethylamine (0.12 mol) in anhydrous benzene (100 ml) was added dropwise a solution of acryloyl chloride (0.1 mol) or its congener (0.1 mol) in anhydrous benzene (50 ml). After being refluxed for 2 h, the mixture was cooled and filtered to remove triethylamine hydrochloride. The filtrate was evaporated to give a residue which was purified by either distillation or recrystallisation with a suitable solvent to afford the corresponding *N*-naphthylacrylamide (1)—(6) (Table 1).

Methyl 3-(N-*Methyl*-2-*methylacrylamido*)-1-*naphthoate* (6d).—To a stirred suspension of the methacrylamide (6c) (6 g) and sodium hydride (2 g) in anhydrous benzene was added methyl iodide (4 g) at room temperature. The resulting mixture was warmed under reflux for 2 h, then diluted with benzene, washed with water, and dried. The solvent was evaporated to give the *N*-methylmethacrylamide (6d) (4.3 g, 73%) as crystals (Table 1).

General Procedure for Irradiation of N-*Naphthylacrylamides* (1)—(6).—A 0.005—0.02M solution of each of the acrylamides (1)—(6) in methanol, benzene, or acetic acid was irradiated as

Table 1. Enamides (1)—(6) *

Compd.	ν_{max}/cm^{-1} ($CHCl_3$) (NCO)	M.p. [B.p.] (°C) (solvent)	Formula	Analysis (%) † C	H	N
(1a)	3 430 (NH), 1 695, 1 680	140—142 (MeOH)	$C_{13}H_{11}NO\cdot 1/8H_2O$	78.3	5.75	7.0
				(78.25	5.7	7.0)
(1b)	1 653, 1 622	[150; 2 mmHg]	$C_{14}H_{13}NO$	79.35	6.15	6.55
				(79.6	6.2	6.65)
(2a)	3 420 (NH), 1 675	225—227 (MeOH)	$C_{19}H_{15}NO$	83.65	5.85	5.35
				(83.5	5.55	5.15)
(2b)	1 650	87—89 (C_6H_{12})	$C_{20}H_{17}NO$	83.65	6.1	4.95
				(83.6	5.95	4.9)
(3a)	3 430 (NH), 1 675	114—116 (MeOH)	$C_{14}H_{13}NO$	79.6	6.4	6.7
				(79.6	6.2	6.65)
(3b)	1 645	102—104 (Et_2O)	$C_{15}H_{15}NO$	80.15	6.85	6.35
				(79.95	6.7	6.2)
(4a)	3 430 (NH), 1 690	122—124 (MeOH)	$C_{13}H_{11}NO$	79.3	5.75	7.25
				(79.15	5.6	7.1)
(4b)	1 651	[170; 2 mmHg]	$C_{14}H_{13}NO$	79.3	6.5	6.6
				(79.6	6.2	6.65)
(5)	1 653	[180; 1 × 10^{-3} mmHg]	$C_{20}H_{17}NO$	83.35	6.0	4.7
				(83.6	5.95	4.9)
(6a)	3 450 (NH), 1 680	136—139 (lit.,[11] 138.5—139 °C)				
(6b)	1 620	68—71 (Et_2O)	$C_{15}H_{15}NO$	79.85	6.75	6.25
				(79.95	6.7	6.2)
(6c)	3 450 (NH), 1 710 (CO_2Me), 1 673	111.5—112.5 (Et_2O)	$C_{16}H_{15}NO_3$	70.95	5.65	5.05
				(71.35	5.6	5.2)
(6d)	1 720 (CO_2Me), 1 625	[220; 1 mmHg]	$C_{17}H_{17}NO_3$	72.2	6.2	4.7
				(72.05	6.05	4.95)

* Yields were good (>70%) in all cases. † Required values in parentheses.

Table 2. Lactams (7a), (8a), (9a and b), (10a and b), (11), and (12a—d)

Compd.	Yield (%)	Solvent for irradiation	M.p. [B.p.] (°C) (solvent)	Formula	Analysis (%) * C	H	N
(7a)	25	C_6H_6–AcOH (1 : 1)	145—147 (MeOH)	$C_{13}H_{11}NO$	79.05	5.85	7.05
					(79.15	5.6	7.1)
(8a)	12	C_6H_6–AcOH (1 : 10)	200—202 (MeOH)	$C_{19}H_{15}NO$	83.8	5.85	5.1
					(83.5	5.55	5.15)
(9a)	40	C_6H_6–AcOH (10 : 1)	191—192 (MeOH)	$C_{14}H_{13}NO$	79.4	6.25	6.5
					(79.6	6.2	6.65)
(9b)	20	C_6H_6	[180; 0.4 mmHg]	$C_{15}H_{15}NO$	79.95	6.8	6.15
					(79.95	6.7	6.2)
(10a)	50	C_6H_6–EtOH (9 : 1)	242—243 (MeOH)	$C_{13}H_{11}NO$	79.0	5.75	7.1
					(79.15	5.6	7.1)
(10b)	33	MeOH	131—132 (C_6H_{12})	$C_{14}H_{13}NO$	79.55	6.1	6.55
					(79.6	6.2	6.65)
(11)	65	MeOH	[210; 1 × 10^{-3} mmHg]	$C_{20}H_{17}NO$	83.5	5.85	4.7
					(83.6	5.95	4.9)
(12a)	40	AcOH	180—182 (Et_2O)	$C_{14}H_{13}NO$	79.2	6.25	6.7
					(79.6	6.2	6.65)
(12b)	50	C_6H_6	117—118 (Et_2O)	$C_{15}H_{15}NO$	79.7	6.65	6.25
					(79.95	6.7	6.2)
(12c)	43	C_6H_6	195—197 (MeOH)	$C_{16}H_{15}NO_3$	71.3	5.7	5.0
					(71.35	5.6	5.2)
(12d)	48	C_6H_6	143—146 (MeOH)	$C_{17}H_{17}NO_3$	72.35	6.15	4.95
					(72.05	6.05	4.95)

* Required values in parentheses.

described previously [7] for several hours in a quartz vessel until disappearance of the starting acrylamide was indicated by t.l.c. The solvent was removed and the residue was chromatographed on alumina or silica gel to give the photocyclised products (7a), (8a), (9a and b), (4a and b), (5), and (6a, b, and c) (Tables 2 and 3).

Nitration of the Lactam (12d).—(a) 90% Nitric acid (1 ml) was added dropwise to the stirred lactam (12d) (100 mg) with ice-cooling, and the mixture was then stirred at room temperature for 3 min. The reaction mixture was then poured onto crushed ice. The precipitated product was collected and recrystallised from methanol to afford *methyl* 2,4-*dimethyl*-8,10-*dinitro*-3-*oxo*-1,2,3,4-*tetrahydrobenzo*[f]*quinoline*-6-*carboxylate* (13a) (40 mg, 30%) as yellow crystals, m.p. 173—175 °C; $\nu_{max.}$ 1 730 (CO_2Me), 1 690 (NCO), and 1 535 cm^{-1} (NO_2); δ 10.17 (1 H, d, *J* 2.5 Hz, 9-H), 8.68 (1 H, d, *J* 2.5 Hz, 7-H), 8.51 (1 H, s, 5-H), 4.11 (3 H, s, CO_2Me), 3.55 (3 H, s,

Table 3. Spectral data for photocyclisation products (7)—(12)

Compd.	ν_{max}/cm^{-1} ($CHCl_3$)	δ ($CDCl_3$)
(7a)	3 420 (NH), 1 680 (NCO)	8.80 (1 H, br s, NH), 3.33—2.58 (4 H, m, 3- and 4-H_2)
(8a)	3 400 (NH), 1 680 (NCO)	9.00 (1 H, br s, NH), 4.50 (1 H, t, *J* 9 Hz, CH), 3.07 (2 H, d, *J* 9 Hz, 3-H)
(9a)	3 420 (NH), 1 675 (NCO)	9.00 (1 H, br s, NH), 1.43 (3 H, d, *J* 6 Hz, CMe)
(9b)	1 660 (NCO)	3.57 (3 H, s, NMe), 1.63 (3 H, d, *J* 6 Hz, CMe)
(10a)	3 420 (NH), 1 680 (NCO)	8.80 (1 H, br s, NH), 7.05 (1 H, d, *J* 9 Hz, 6-H)
(10b)	1 660 (NCO)	3.45 (3 H, s, NMe)
(11)	1 665 (NCO)	4.96 (1 H, t, *J* 4.5 Hz, 1-H), 3.10 (2 H, d, *J* 4.5 Hz, 2-H_2), 3.45 (3 H, s, NMe)
(12a)	1 690 (NCO)	9.22 (1 H, br s, NH), 1.40 (3 H, d, *J* 7 Hz, CMe)
(12b)	1 660 (NCO)	8.66 (1 H, br s, NH), 3.43 (3 H, s, NMe), 1.33 (3 H, d, *J* 7 Hz, CMe)
(12c)	3 450 (NH), 1 710 (CO_2Me), 1 680 (NCO)	8.78 (1 H, m, 7-H), 7.63 (1 H, s, 5-H), 3.96 (3 H, s, CO_2Me), 1.38 (3 H, d, *J* 7 Hz, CMe)
(12d)	1 715 (CO_2Me), 1 660 (NCO)	8.88 (1 H, m, 7-H), 7.98 (1 H, s, 5-H), 4.07 (3 H, s, CO_2Me), 3.53 (3 H, s, NMe), 1.38 (3 H, d, *J* 7 Hz, CMe)

NMe), and 1.25 (3 H, d, *J* 6.5 Hz, CMe) (Found: C, 54.95; H, 4.15; N, 11.00. $C_{17}H_{15}N_3O_7$ requires C, 54.7; H, 4.05; N, 11.25%).

(b) Nitration of the lactam (12d) (500 mg) with 60% nitric acid (5 ml) was carried out as in method (a). The crude nitrated product was recrystallised from benzene to afford *methyl* 2,4-*dimethyl*-8-*nitro*-3-*oxo*-1,2,3,4-*tetrahydrobenzo*[f]-*quinoline*-6-*carboxylate* (13b) (200 mg, 35%) as yellow crystals, m.p. 209—210 °C; $\nu_{max.}$ 1 720 (CO_2Me), 1 675 (NCO), and 1 540 cm^{-1} (NO_2); δ 9.90 (1 H, d, *J* 2.5 Hz, 7-H), 8.37 (1 H, dd, *J* 9.5 and 2.5 Hz, 9-H), 8.18 (1 H, s, 5-H), 8.13 (1 H, d, *J* 9.5 Hz, 10-H), 4.08 (3 H, s, CO_2Me), 3.53 (3 H, s, NMe), and 1.40 (3 H, d, *J* 6.5 Hz, CMe) (Found: C, 63.95; H, 5.1; N, 7.75. $C_{17}H_{16}N_2O_5 \cdot 1/3C_6H_6$ requires C, 64.05; H, 5.35; N, 7.85%).

The mother liquor from the above recrystallisation was condensed to afford *methyl* 2,4-*dimethyl*-10-*nitro*-3-*oxo*-1,2,3,4-*tetrahydrobenzo*[f]*quinoline*-6-*carboxylate* (13c) (50 mg, 27%) as pale yellow crystals (from methanol), m.p. 187—188 °C; $\nu_{max.}$ 1 725 (CO_2Me), 1 675 (NCO), and 1 520 cm^{-1} (NO_2); δ 9.15 (1 H, dd, *J* 8.5 and 1.5 Hz, 9-H), 8.08 (1 H, s, 5-H), 7.92 (1 H, dd, *J* 7.5 and 1.5 Hz, 7-H), 7.53 (1 H, dd, *J* 8.5 and 7.5 Hz, 8-H), 4.05 (3 H, s, CO_2Me), 3.52 (3 H, s, NMe), and 1.26 (3 H, d, *J* 6.5 Hz, CMe) (Found: C, 62.3; H, 5.0; N, 8.5. $C_{17}H_{16}N_2O_5$ requires C, 62.2; H, 4.9; N, 8.55%).

(c) Nitration of the lactam (12d) (1 g) with a mixture of 70% nitric acid (2 ml) and acetic anhydride (2 ml) was carried out at room temperature with stirring for 10 min. The mixture was then diluted with water and the aqueous layer was extracted with chloroform. The extract was washed with water, dried, and evaporated. Recrystallisation of the residue as in case (b) afforded the nitrated lactams (13b) (200 mg, 17%) and (13c) (650 mg, 56%).

Methyl 10-*Amino*-2,4-*dimethyl*-3-*oxo*-1,2,3,4-*tetrahydrobenzo*[f]*quinoline*-6-*carboxylate* (14).—To a solution of the lactam (13c) (1.4 g) in a mixture of methanol and dioxane (8 : 2; 100 ml) were successively added dropwise Raney nickel (500 mg) and a solution of hydrazine hydrate (0.7 ml) in methanol (1 ml). After the mixture had been refluxed for 0.5 h, the Raney nickel was filtered off and the filtrate was evaporated to give an oil which crystallised with time and which was recrystallised from diethyl ether–methanol to afford the *amine* (14) (1.1 g, 87%) as yellow crystals, m.p. 154—156 °C; $\nu_{max.}$ 1 715 (CO_2Me) and 1 665 cm^{-1} (NCO); δ 8.23 (1 H, dd, *J* 9 and 1.5 Hz, 7-H), 7.81 (1 H, s, 5-H), 7.32 (1 H, dd, *J* 9 and 7.5 Hz, 8-H), 6.80 (1 H, dd, *J* 7.5 and 1.5 Hz, 9-H), 3.99 (3 H, s, CO_2Me), 3.92 (2 H, br s, NH_2), 3.62 (3 H, s, NMe), and 1.27 (3 H, d, *J* 7 Hz, CMe) (Found: C, 68.2; H, 6.15; N, 9.3. $C_{17}H_{18}N_2O_3$ requires C, 68.45; H, 6.1; N, 9.4%).

Methyl 10-*Acetamido*-2,4-*dimethyl*-3-*oxo*-1,2,3,4-*tetrahydrobenzo*[f]*quinoline*-6-*carboxylate* (15).—A mixture of the amine (14) (1.1 g), acetic anhydride (1 ml), and pyridine (3 ml) was kept at room temperature overnight. Then the reaction mixture was condensed *in vacuo* and the resulting residual solid was recrystallised from methanol to afford the *acetamide* (15) (700 mg, 56%) as crystals, m.p. 205—208 °C; $\nu_{max.}$ 3 430 (NH), 1 705 (CO_2Me), and 1 680—1660 cm^{-1} (NCO); δ 7.88 (1 H, br s, NH), 4.00 (3 H, s, CO_2Me), 3.33 (3 H, s, NMe), 2.22 (3 H, br s, Ac), and 1.22 (3 H, d, *J* 6.5 Hz, CMe) (Found: C, 66.9; H, 6.0; N, 8.05. $C_{19}H_{20}N_2O_4$ requires C, 67.05; H, 5.9; N, 8.25%).

1-*Acetamido*-7,9-*dimethyl*-4,5,7,8,9,10-*hexahydroindolo*-[4,3-fg]*quinoline*-5,8-*dione* (17).—According to the procedure given for (12d), nitration of the lactam (15) (700 mg) in a mixture of 70% nitric acid (2 ml) and acetic anhydride (2 ml) gave the nitrated compound (16) which was, without purification, reduced with Raney nickel and hydrazine hydrate in dioxane (60 ml) as in the case of (13c). After the Raney nickel had been filtered off, the filtrate was evaporated and then acidified by the addition of 10% hydrochloric acid. The precipitated crystals were collected and recrystallised from methanol to give the *indoloquinoline* (17) (160 mg, 24%) as pale yellow crystals, m.p. >300 °C; $\nu_{max.}$ (Nujol) 3 200 (NH), 1 690—1 640 cm^{-1} (3 × NCO); δ[$(CD_3)_3SO$] 7.87 (1 H, s, 6-H), 7.25 and 6.91 (each 1 H, d, *J* 6.5 Hz, together 2- and 3-H), 3.43 (3 H, s, NMe), 2.10 (3 H, s, Ac), and 1.18 (3 H, d, *J* 6.5 Hz, CMe) (Found: M^+, 323.126. $C_{18}H_{17}N_3O_3$ requires *M*, 323.127).

2-*Methyl*-N-(2-*oxo*-1,2-*dihydrobenz*[cd]*indol*-4-*yl*)*acrylamide* (19a).—According to the general procedure described above, acylation of 4-amino-1,2-dihydrobenz[*cd*]indol-2-one (18a) (2.31 g) with methacryloyl chloride (1.37 g) in dimethylformamide (50 ml) gave the *methacrylamide* (19a) (1.45 g, 46%) as yellow needles (from diethyl ether–methanol), m.p. 221—223 °C; $\nu_{max.}$ (Nujol) 3 270, 3 115 (NH), and 1 680 cm^{-1} (2 × NCO); δ [$(CD_3)_2SO$] 10.72 (1 H, br s, NH), 10.18, (1 H, br s, NH), 5.97 and 5.62 (each 1 H, m, together H_2C=C), and 2.05 (3 H, s, CMe) (Found: C, 70.2; H, 4.7; N, 11.15. $C_{15}H_{12}N_2O_2 \cdot 1/5H_2O$ requires C, 70.4; H, 4.85; N, 10.95%).

4-*Methylamino*-1,2-*dihydrobenz*[cd]*indol*-2-*one* (18b).—A solution of 4-amino-1,2-dihydrobenz[*cd*]indol-2-one (18a) (6.7 g) and benzaldehyde (10 ml) in anhydrous methanol (600 ml) was refluxed for 5 h. After the mixture had been concentrated to half its original volume, the precipitated crystals were collected and recrystallised from methanol to give 4-benzylideneamino-1,2-dihydrobenz[*cd*]indol-2-one (9 g, 93%) as yellow crystals, m.p. 193—195 °C (lit.,[10] 199—200 °C).

Reduction of the Schiff's base with sodium borohydride gave the 4-benzylamino compound (8 g, 90%) as crystals (from methanol), m.p. 171—173 °C. A solution of the 4-benzylamino compound (1 g) and methanesulphonyl fluoride (1 g) in acetonitrile (40 ml) was stirred at room temperature for 3 h. After evaporation of the solvent under reduced pressure, the residue was dissolved in ethyl acetate and the resulting solution was washed in turn with aqueous sodium hydrogen carbonate and water, dried, and evaporated. The residual solid was recrystallised from methanol to afford 4-*benzylmethylamino*-1,2-*dihydrobenz*[cd]*indol*-2-*one* (700 mg, 60%) as yellow needles, m.p. 153—155 °C (Found: C, 79.35; H, 5.80; N, 9.65. $C_{19}H_{16}N_2O$ requires C, 79.15; H, 5.60; N, 9.75%).

A solution of the 4-benzylmethylamino compound (2.7 g) in acetic acid (200 ml) and conc. hydrochloric acid (1 ml) was hydrogenated over 40% palladium–carbon (500 mg) under hydrogen (5 atm) at room temperature for 3 h. The catalyst was filtered off and the filtrate was evaporated to give an oil which was dissolved in ethyl acetate and the resulting solution was washed in turn with aqueous sodium hydrogen carbonate and water, dried, and evaporated. The residual solid was recrystallised from methanol to give 4-methylamino-1,2-dihydrobenz[*cd*]indol-2-one (18b) (1.35 g, 88%) as yellow crystals, m.p. 210—215 °C (lit.,[10] 218—220 °C).

2,N-*Dimethyl*-N-(2-*oxo*-1,2-*dihydrobenz*[cd]*indol*-4-*yl*)*acrylamide* (19b).—According to the general procedure, acylation of 4-methylamino-1,2-dihydrobenz[*cd*]indol-2-one (18b) (2.2 g) with methacryloyl chloride (1.2 g) in benzene (200 ml) gave the *methacrylamide* (19b) (2.08 g, 70%) as pale yellow crystals (from methanol–diethyl ether), m.p. 209—211 °C; $\nu_{max.}$ 3 470 (NH) and 1 705—1 640 (2 × NCO) cm^{-1}; δ 9.87 (1 H, br s, NH), 5.07 (2 H, br, H_2C=C), 3.48 (3 H, s, NMe), and 1.83 (3 H, s, CMe) (Found: C, 71.85; H, 5.45; N, 10.3. $C_{16}H_{14}N_2O_2$ requires C, 72.15; H, 5.3; N, 10.5%).

7,9-*Dimethyl*-4,5,7,8,9,10-*hexahydroindolo*[4,3-fg]*quinoline*-5,8-*dione* (20).—According to the general procedure, irradiation of the methacrylamide (19b) (600 mg) in a mixture of benzene and acetic acid (15 : 1; 800 ml) for 96 h gave the *lactam* (20) (250 mg, 42%) as pale yellow needles (from methanol–benzene), m.p. >300 °C; $\nu_{max.}$ (Nujol) 1 710 and 1 655 cm^{-1} (2 × NCO); δ[$(CD_3)_2SO$] 10.63 (1 H, br s, NH), 7.82 (1 H, s, 6-H), 3.45 (3 H, s, NMe), and 1.25 (3 H, d, *J* 7 Hz, CMe) (Found: C, 71.95; H, 5.4; N, 10.45. $C_{16}H_{14}N_2O_2$ requires C, 72.15; H, 5.3; N, 10.5%).

4-*Acetyl*-7,9-*dimethyl*-4,5,7,8,9,10-*hexahydroindolo*[4,3-fg]*quinoline* (21).—To an ice-cooled solution of the lactam (20) (80 mg) in a mixture of anhydrous diethyl ether–tetrahydrofuran (1 : 1; 40 ml) was added lithium aluminium hydride (80 mg) in small portions. The mixture was heated under reflux for 1 h. Treatment in the usual way gave the corresponding amine which was, without purification, acetylated with acetic anhydride to afford the acetate (21) (40 mg, 50%) as yellow crystals (from methanol), m.p. 205—208 °C; $\nu_{max.}$ 1 680 cm^{-1} (NCO); δ 2.97 (3 H, s, NMe), 2.27 (3 H, br s, Ac), and 1.12 (3 H, d, *J* 6 Hz, CMe) (Found: C, 76.7; H, 7.15; N, 9.85. $C_{18}H_{20}N_2O$ requires C, 77.1; H, 7.2; N, 10.0%).

Acknowledgements

The authors thank the Ministry of Education, Science, and Culture (Japan) for a research grant.

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Received 1*st June* 1983; *Paper* 3/880