Pergamon

Tetrahedron Vol. 50, No. 47, pp. 13433-13448, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00862-0

Functionalisation of the Alkoxy Group of Alkyl Aryl Ethers. Demethylation, Alkylthiolation and Reduction of 5-Methoxyindoles

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Abstract: In the presence of AlX_3-RSH three kinds of reactions may take place with 5-methoxy indoles : demethylation, alkylthiolation and reduction. The two latter reactions have never been observed to the present, with such reagents. Considerable improvement in the selective demethylation was found when $PhCH_2SH$ replaced EtSH previously used in such transformations. Factors leading to selective alkylthiolations or reductions are shown and mechanisms are proposed to explain these new reactions.

Introduction

As part of a program aiming at the synthesis of 5-hydroxyindoles with potential pharmacological properties we were confronted with the demethylation of the corresponding methoxy derivatives.

Demethylation of methyl ethers, and particularly aryl methyl ethers is an important reaction which gives rise to a large number of investigations leading to numerous demethylation reagents. Only a few of them have been used in the indole series and for the most part demethylations are performed either with the very expensive BBr_3[1] or with $AlCl_3$[2] or HBr.[3]

Using the above-mentioned techniques, with a number of substrates we were interested in, these reagents led to disappointing results. We thus decided to turn toward aluminum halides associated with thiols[4] which curiously have never been investigated in the indoles series. A number of exploratory experiments[5] showed that AlX_3-RSH reagents could be of interest to perform such demethylations. Very recently, and independently, such a reaction was incidentally observed during a desulfurization in indoles series.[6]

During our preliminary studies, besides the demethylation we also observed other reactions of potential

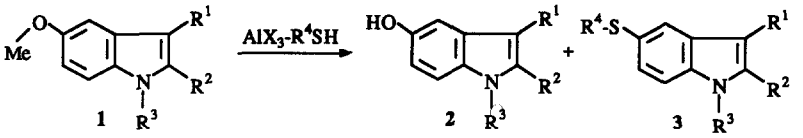
synthetic interest such as alkylthiolations and reductions. To the best of our knowledge such reactions have never been observed in the usual demethylations performed with aryl methyl ethers.

In the present paper we describe in detail the reactions performed with two families of 5-methoxyindole derivatives. The influence of the main factors was determined and the demethylation themselves improved.

Results and discussion

With a first series of methoxyindoles the only products formed were the corresponding hydroxy or alkylthioindoles (Scheme 1).

Scheme 1



In Table I are gathered the most significant results of a systematic study performed with compound **1a**.

Table I

Run	Substrate	R1	R2	R3	R4	AlX_3	T°C	Time (h)	Isolated yields % 2	3	Method
1					-	$AlCl_3$	0/RT	3/12	13	-	B
2					Et	$AlCl_3$	0	3	75	-	A
3					Et	$AlCl_3$	0	5	75	15	A
4					Et	$AlBr_3$	0/RT	5/12	91	-	A
5					Et	AlI_3	0/RT	5/12	53	-	A
6					Ph	$AlCl_3$	0	5	70	-	A
7	1a	$(CH_2)_4$		Me	$PhCH_2$	$AlCl_3$	0	5	100	-	A
8					Et	$AlCl_3$	0/RT	3/12	75	25	B
9					Et	$AlCl_3$	0/RT	3/48	20	78	B
10					Et	$AlBr_3$	0/RT	5/96	40	20	B
11					Ph	$AlCl_3$	0/RT	3/48	73	-	B
12					Ph	$AlBr_3$	0/RT	3/198	50	-	B
13					$PhCH_2$	$AlCl_3$	0/RT	3/504	71	-	B

From the systematic study the following interesting features emerged :

Most of the thiol excess was recovered after the work up.

$AlCl_3$ alone was inefficient while in combination with thiols the demethylation took place easily.

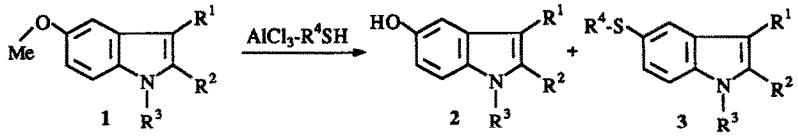
For a given thiol, $AlBr_3$, which had been found more reactive than $AlCl_3$[4a] appeared less efficient in the formation of **3** and thus more selective to perform the demethylation.

For a given aluminum halide the results obtained reflect the nucleophilic trend of the thiols : EtSH >

$PhCH_2SH$ > PhSH. Thus EtSH was very efficient in the formation of **2** as well as **3**. PhSH showed no tendency to form **3** and was much less efficient in the demethylation. $PhCH_2SH$ was just nucleophilic enough to easily perform very selective demethylation without alkylthiolation.

With these results in hand we examined the behaviour of a number of representative indole derivatives using the $AlCl_3$-RSH (R = Et, $PhCH_2$) systems (Table II).

Table II



Run	Substrate	R1	R2	R3	R4	T°C	Time (h)	Isolated yields % 2	3	Method
1	**1b**	$(CH_2)_4$		H	$PhCH_2$	0	2.5	96[a]	-	A
2					Et	0/RT	3/20	ε	71	B
3	**1c**	$(CH_2)_5$		Me	$PhCH_2$	0	3.5	97	-	A
4					Et	0/RT	3/144	32	53	B
5	**1d**	$(CH_2)_5$		H	$PhCH_2$	0	2.5	100	-	A
6					Et	0/RT	3/25	ε	92	B
7	**1e**	$(CH_2)_6$		Me	$PhCH_2$	0	1.5	96	-	A
8					Et	0/RT	3/144	ε	80	B
9	**1f**	$(CH_2)_6$		H	$PhCH_2$	0	1.5	99	-	A
10					Et	0	3	-	97	B
11	**1g**	$(CH_2)_{10}$		Me	$PhCH_2$	0	1.5	87	-	A
12					Et	0/RT	3/48	ε	80	B
13	**1h**	$(CH_2)_{10}$		H	$PhCH_2$	0	2	95[a]	-	A
14					Et	0/RT	3/20	ε	83	B
15	**1i**	H	Me	Me	$PhCH_2$	0	2	80	-	A
16					Et	0/RT	3/192	26	-	B
17	**1j**	H	2-thienyl	Me	$PhCH_2$	0	2.5	96	-	A
18					Et	0/RT	3/156	67	b)	B
19	**1k**	n-C_5H_{11}	H	H	Et	0/RT	3/3.5	-	76	B

a) Sensitive to air and turn black rapidly.
b) Small amount of product detected by GCMS analysis.

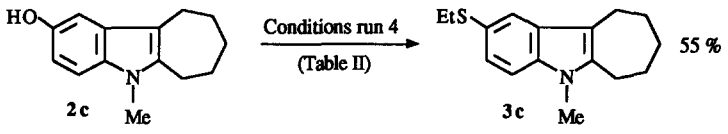
As far as demethylation was concerned, it appeared that $AlCl_3$-$PhCH_2SH$ led to the best results, the corresponding hydroxyindoles being obtained in excellent yields under very mild conditions. Interestingly, such a system has never been used before and these results show how sensitive to small electronic effects these reactions are. With method A aiming at performing only demethylation, experiments with EtSH were performed but not reported in Table II for sake of clarity. In every case, it appeared that EtSH may be used but in most of cases yields are lower than with $PhCH_2SH$.

Still more intringuing were the alkylthiolations, the position of which was unequivocally determined by an X-ray study (see experimental part). Indeed while ethylthioindoles were obtained in good to excellent yields with tricyclic indoles (**1a-1h**), no such compounds were isolated with **1i** and only a few percent with **1j**. Formally the

only difference between **1i** and **1a** to **1h** was the presence of an alkyl group on the C_3 position of the latter. We thus suspected that such a substitution favoured the alkylthiolations. This hypothesis was verified with **1k** for which ethylthiolation took place very easily and in very good yields. In fact **1k** was more reactive than indoles **1a** to **1h** and we concluded that the presence of a 2-alkyl substituent was unfavourable for condensations. Furthermore N-methylated indoles appeared less reactive than their corresponding N-unsubstituted substrates.

Finally it was of interest to know the origin of **3** which, *a priori*, could be formed either directly from **1** or from **2**. In fact examination of the results of Tables I and II as well as monitoring of the reaction by gpc led us to suppose that hydroxy indoles **2** should be the intermediate in the alkylthiolations. This conclusion was verified with **2c** which gives **3c** when using the experimental conditions of run 4 (Table II) as given in Scheme 2.

Scheme 2



According to Casnati and his collaborators[7] it is clear that aluminum alkoxides are the key intermediates during such a transformation.

With all the above informations in hand, a number of mechanistic explanations, summarized in Scheme 3, may be formulated to account for the results obtained.

For sake of simplicity the complexes formed between $AlCl_3$ and R^4SH which apparently do not intervene during these reactions, have not been represented.

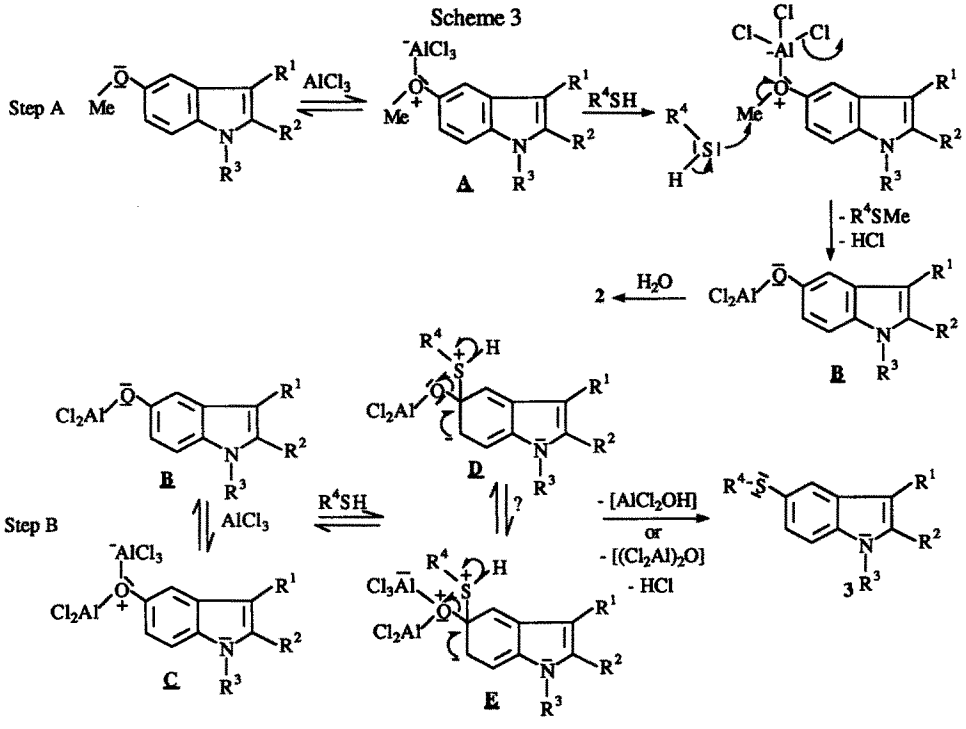
The mechanism of step A is that proposed by Fujita and his collaborators.[4] R^4SH plays the role of a nucleophile in step A as well as in step B so that competition may take place between demethylation and alkylthiolation if the nucleophilicity of the thiol is strong enough. However this nucleophilicity must be sufficient to allow step A to be performed at a reasonable rate. Such a behaviour of R^4SH in steps A and B is well reflected by the relative reactivity found with ethyl, benzyl and benzene thiols.

A priori, step B is not an easy nucleophilic substitution since first it necessitates the nucleophilic attack on a benzene ring not activated by an electron-withdrawing group and second it requires breaking the rather strong aryl-oxygen bond. This situation is well reflected by the fact that $AlCl_3$ was necessary to perform the alkylthiolation. Thus complex C must be the main, if not the only, intermediate of the substitution. Under such conditions the driving force of the reaction should be due to the negative inductive effect of the oxygen leading to a labilization of the carbon-oxygen bond and to the formation of the thermodynamically favoured aluminum-oxygen bond.

Based on the above hypothesis and observations, it must be concluded that the products of such reactions must be influenced by small electronic effects.

Thus electron enrichment of the benzene ring must favour the formation of complex C but not favour the already difficult nucleophilic attack of the thiol which must be the limiting step. On the other hand, electron-donating effects of substituents are well transmitted to the benzene ring when they are situated on the nitrogen and above all on the C_2 position of the indole. Such an effect remains much more localized in the five-membered ring when the substituents are on the C_3 position, and even counter balances the electron-donating effect of a C_2 substituent.

Scheme 3



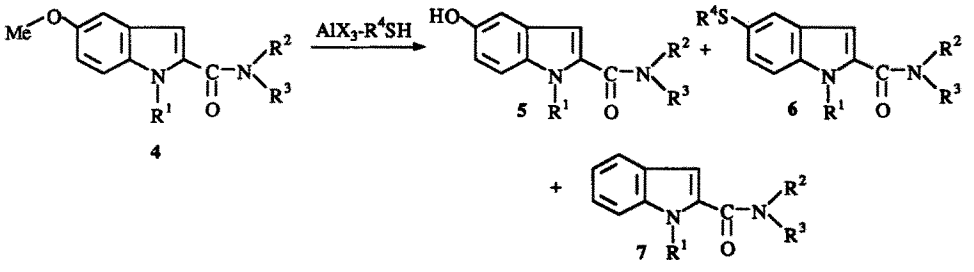
These proposed mechanisms completely agree with the results obtained. Moreover they lead to the conclusion that the presence of an electron-withdrawing group on the C_2 position must strongly favour the alkylthiolation while on the C_3 position such an influence must not be so important.

In fact we shall see below that such a prediction has been verified but that another unexpected interesting reaction was also favoured and competed with the expected transformation.

Indeed we encountered the opportunity of verifying our hypothesis when, for pharmaceutical purposes, we wanted to prepare 5-hydroxy indole amides from the corresponding methoxy derivatives easily obtained from the commercially available 5-methoxy indole 2-carboxylic acid.

Exploratory experiments rapidly showed that the most general reaction taking place with this second family of indole derivatives corresponded to the reaction summarized in Scheme 4.

Scheme 4



The reduction of **4** under such conditions was also unprecedented.

The main results of which have been illustrated in Table III with **4a** showed that the general observation previously made was maintained.

Table III

Run	Substrate	R^1	R^2	R^3	R^4	AlX_3	T°C	Time (h)	Isolated yields % **5**	**6**	**7**	Method
1					Et	$AlCl_3$	0	2	46	26	a)	A
2					Et	$AlCl_3$	0/RT	3/72	-	-	69	B
3					Et	$AlBr_3$	0	3	21	25	a)	A
4					Et	$AlBr_3$	0/RT	3/72	-	-	63	B
5					Ph	$AlCl_3$	0	3	10	-	-	A
6	**4a**	Me	Ph	H	Ph	$AlBr_3$	0	2	50	-	9	A
7					Ph	$AlCl_3$	0/RT	3/12	60	-	40	B
8					$PhCH_2$	$AlCl_3$	0	2	78	a)	a)	A
9					Ph	$AlCl_3$	0/RT	3/60	-	-	60	B
10					Ph	$AlBr_3$	0/RT	3/24	-	-	67	B
11					Ph	$AlBr_3$	0/RT	3/60	-	-	82	B

a) Small amount of product detected by GCMS analysis.

Thus benzyl thiol continued to be the best reagent to obtain the hydroxy derivatives **5**. EtSH had to be preferred when alkylthiolation was desired although the formation of the reduction product **7** was difficult to avoid. One new interesting point was the behaviour of thiophenol which combined with AlX_3 led very efficiently to the reduced substrate **7**. In fact $AlBr_3$ led to cleaner reactions and was thus preferred to $AlCl_3$.

We then examined the behaviour of a number of representative indole amide derivatives using these AlX_3-R^4SH systems (Table IV).

From the overall data of Table IV it appears that using the appropriate experimental conditions, demethylations and reductions could be selectively performed in good yields. Selective thioalkylations, although possible, were less easily obtained. Unreported experiments performed with **4c** and **4i** showed that, even using a method B usually appropriate to the formation of **6**, led only to **5** (35 to 50 %) and to inseparable mixtures of **6** (20-25 %) and **7** (20-22 %) as evaluated by GCMS and ^1H NMR analysis.

Table IV

Run	Substrate	R^1	R^2	R^3	R^4	AlX_3	T°C	Time (h)	Isolated yields % 5	6	7	Method
1					$PhCH_2$	$AlCl_3$	0	3	70	b)	-	A
2	**4b**	H	Ph	Me	Et	$AlCl_3$	0	4.5	15	55	-	B
3					Ph	$AlBr_3$	0/RT	3/60	-	-	78.5	B
4					$PhCH_2$	$AlCl_3$	0	5	70	b)	a)	A
5	**4c**	Me	Ph	Me	Et	$AlCl_3$	0	3	50	b)	a)	A
6					Et	$AlCl_3$	0/RT	3/12	-	-	50	B
7					Ph	$AlBr_3$	0/RT	3/48	-	-	61	B
8					$PhCH_2$	$AlCl_3$	0	5	63	b)	-	A
9	**4d**	H	Ph	n-C_4H_9	Et	$AlCl_3$	0	5	38	55	-	A
10					Ph	$AlBr_3$	0/RT	3/30	-	-	63	B
11					$PhCH_2$	$AlCl_3$	0	2	71	b)	a)	A
12	**4e**	Me	Ph	n-C_4H_9	Et	$AlCl_3$	0	3	83	a)	-	B
13					Et	$AlCl_3$	0/RT	3/2	45	43	-	B
14					Ph	$AlBr_3$	0/RT	3/72	-	-	88	B
15					$PhCH_2$	$AlCl_3$	0	2.5	70.5	b)	-	A
16	**4f**	H	Ph	n-C_6H_{13}	Et	$AlCl_3$	0	3	55	43	-	B
17					Ph	$AlBr_3$	0/RT	3/48	-	-	50	B
18					$PhCH_2$	$AlCl_3$	0	2.5	77	b)	-	A
19	**4g**	Me	Ph	n-C_6H_{13}	Et	$AlCl_3$	0/RT	3/7	45	50	-	B
20					Ph	$AlBr_3$	0/RT	3/48	-	-	80	B
21					$PhCH_2$	$AlCl_3$	0	3	87	-	-	A
22	**4h**	H	Ph	n-C_8H_{17}	Et	$AlCl_3$	0	3	30	70	-	B
23					Ph	$AlBr_3$	0/RT	3/50	-	-	73	B
24					$PhCH_2$	$AlCl_3$	0	5	73	-	-	A
25	**4i**	Me	3-ClC_6H_4	Me	Et	$AlCl_3$	0	3	55	-	-	A
26					Ph	$AlBr_3$	0	3	-	-	56	B

a) Small amount of product detected by GCMS analysis and characterized elsewhere.
b) Detected by GCMS analysis.

The successive steps of the transformations were determined thanks to reactions performed with some representative substrates (Scheme 5).

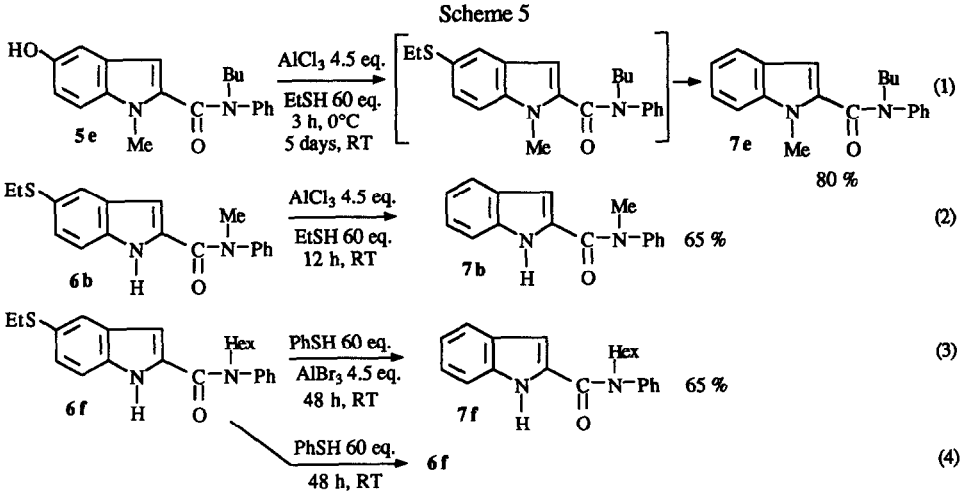
Sampling the reaction medium during the reductions, we observed by gpc the transient formation of the corresponding hydroxy indole.

Reaction (1) confirmed the intermediate formation of hydroxyindole. Moreover the transient formation of the alkylthioindoles was shown. Reactions (2) and (3) confirmed the reduction of the alkylthioindoles with RSH-AlX_3 reagents, and reaction (4) showed that no such a reduction could take place without AlX_3.

Thus it was concluded that the overall scheme of the possible transformations comprised the successive steps : **4** → **5** → **6** → **7**.

We are unable to evaluate the influence of the nature of the substituent borne by the nitrogens of the indole ring or of the amide function. Indeed the yields of the product obtained depend not only on the stereoelectronic effects but also on the stability of the products formed, and we have no information about these parameters.

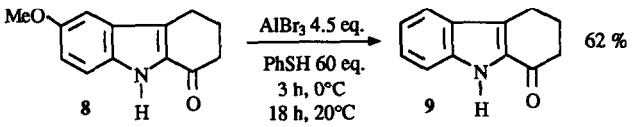
Scheme 5



On the contrary, the influence of the electron-withdrawing group in the C_2 position is clear and supported our hypothesis. Indeed comparison of the data of Tables II and IV shows an increase of the overall reactivity with indole 2-carboxamide **4**. Moreover it also appeared that the electron-withdrawing group strongly favoured the reduction explaining, as a consequence, that in some cases the alkylthioindoles were not easily isolated.

The reaction performed in Scheme 6 confirms this observation.

Scheme 6

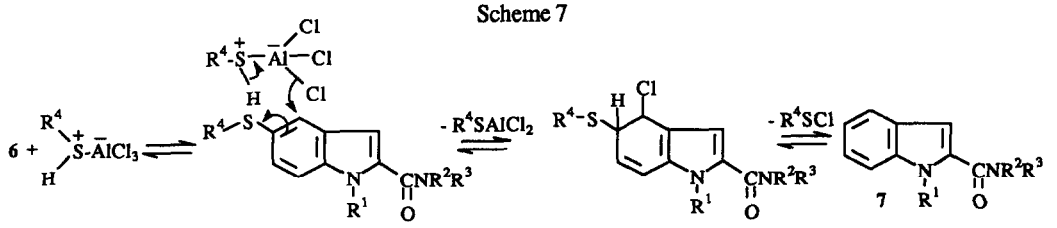


8 easily obtained by arynic cyclisation[8] is a ketonic analogous of **1b** (Table II) which, as the other indoles of this family, was never reduced under these conditions and was destroyed under more drastic ones.

From a mechanistic point of view, demethylations and alkylthiolations must take place as given in Scheme 3. Concerning the reductions it must be recalled that they necessitate the presence of AlX_3 and that the electron empoverishment of the benzene ring was strongly favourable. In other words a nucleophilic attack must take place. On the other hand the reaction medium is not prone to release H^- from any species and a nucleophilic substitution of the thioalkyl group by hydrides appears highly improbable.

Examination of the resonance forms of the substrates which were reduced shows the development of a positive charge on the ortho position of the sulfur atom and leads to tentatively proposing the mechanism of reduction given in Scheme 7.

Scheme 7



Of course the attack of "Cl^-" may also take place on the C_6 position to give the same result.

Conclusion

It has been shown that demethylation of methoxyindoles may be performed with AlX_3-RSH while AlX_3 was not suitable. A systematic study led to the finding that $AlCl_3$-$PhCH_2SH$ was much more efficient than the classical $AlCl_3$-EtSH reagent.

On the other hand, it was found that under appropriate conditions, AlX_3-RSH may also be used to replace a methoxy group by an alkylthio one or by a hydrogen. Such new reactions are under investigation in order to extend their fields of application and to perform selective transformations of polymethoxyaryl derivatives.

Experimental

General Methods. Melting points were determined on a Totoli melting point apparatus and are uncorrected. ^{13}C NMR spectra were recorded with a Bruker AM 400 or a Bruker 300 MHz spectrometer (Attached Proton Test method, APT). ^1H NMR spectra were recorded on a Jeol PMX 60 at 60 MHz, or a Bruker AM 400 instrument at 400 MHz. Me_4Si was the internal standard. Infrared (IR) spectra of thin liquid films between NaCl plates or KBr pellets were recorded with a Perkin-Elmer 841 instrument. X-ray analysis was performed by Centro di Studio C.N.R. per la Strutturistica Diffrattometrica of Parma (Italy). Elemental analyses were performed by CNRS Laboratory (Vernaison) and by E.N.S.C.M. Microanalysis Department of Montpellier. Mass spectra were recorded on Hewlett Packard 5971A instrument. Thin-layer chromatography (TLC) was performed with plates coated with kieselgel G (Merck). The plates were developed with petroleum ether/EtOAc. The silica gels used for column chromatography and flash chromatography were kieselgels of 0.063-0.2 mm and 0.04-0.063 mm particle size, respectively.

Method A : 1 eq. of compound **1** diluted in CH_2Cl_2 (5 ml for 3 mmol) was added dropwise at 0°C to a mixture of 1.5 eq. of AlX_3 and 20 eq. of RSH. After the reaction was stirred half an hour at 0°C, 1.5 eq. of AlX_3 and 20 eq. of RSH were added. The reaction was monitored by gpc (capillary HP1, 6 m) and stopped when the maximum amount of the desired product was reached. The reaction mixture was hydrolysed with HCl 1N at 0°C, and extracted with CH_2Cl_2. The organic layer was washed with water, then with brine, dried over Na_2SO_4, and the solvent removed under vacuum. The products were isolated by flash column chromatography (Kieselgel, 40-63 μ) using eluent (EtOAc/petroleum ether) of progressive polarity (20 to 30 % for amide derivatives and 10 to 20 % for the others).

Method B : Same procedure as described for method A, but after 1 hour, a third portion of 1.5 eq. of AlX_3 and 20 eq. of RSH were added at 0°C.

1,2,3,4-Tetrahydro-6-hydroxy-9-methylcarbazole **2a, $R^1R^2=(CH_2)_4$, R^3=Me**

IR (NaCl) 3356 (OH), 2930-2839 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.00-6.46 (3 H, m, Arom H), 6.00 (1 H, s, OH), 3.30 (3 H, s, NMe), 2.83-2.16 (4 H, s, 2xCH_2), 2.00-1.46 (4 H, s, 2xCH_2). ^{13}C NMR ($CDCl_3$) δ ppm : 148.5 (Arom COH), 136.4 (Arom C), 132.0 (Arom C), 127.4 (Arom C), 109.7 (Arom CH), 108.7 (Arom CH), 108.2 (Arom C), 102.7 (Arom CH), 23.0 (2xCH_2), 21.8 (CH_2), 20.8 (CH_2), 28.6 (NMe). mp 92°C. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.57, H, 7.51, N, 6.95. Found : C, 77.45, H, 7.51, N, 6.86.

6-Ethylthio-1,2,3,4-tetrahydro-9-methylcarbazole **3a, $R^1R^2=(CH_2)_4$, R^3=Me, R^4=Et**

IR (NaCl) 2927-2840 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.5-6.9 (3 H, m, Arom H), 3.5 (3 H, s, NMe), 3.1-2.3 (6 H, q+m, SCH_2+2xCH_2), 2.2-1.5 (4 H, m, 2xCH_2), 1.5-1.0 (t, 3 H, Me). ^{13}C NMR ($CDCl_3$) δ ppm : 136.4 (Arom CS), 135.9 (Arom C), 127.7 (Arom C), 125.3 (Arom CH), 123.6 (Arom C), 122.3 (Arom CH), 108.9 (Arom C), 108.7 (Arom CH), 30.7 (SCH_2), 28.9 (NMe), 23.0 (2xCH_2), 21.9 (CH_2), 20.9 (CH_2), 14.7 (SCH_2CH_3). mp 51°C. Anal. Calcd for $C_{15}H_{19}NS$: C, 73.41, H, 7.80, N, 5.70, S, 13.06. Found : C, 73.64, H, 7.95, N, 5.60, S, 12.91.

1,2,3,4-Tetrahydro-6-hydroxycarbazole **2b, R^1R^2=$(CH_2)_4$, R^3=H**

IR (NaCl) 3386-3300 (NH+OH), 2922-2850 (C-H). ^1H NMR ($CDCl_3$/ DMSO) δ ppm : 9.3 (1 H, s, OH), 7.2-6.4 (4 H, m, Arom H+NH), 2.8-2.3 (4 H, m, 2xCH_2), 2.1-1.6 (4 H, m, 2xCH_2). ^{13}C NMR ($CDCl_3$/DMSO) δ ppm : 148.8 (Arom COH), 133.9 (Arom C), 129.1 (Arom C), 127.0 (Arom C), 109.5 (Arom CH), 108.7 (Arom CH), 106.8 (Arom C), 100.8 (Arom CH), 22.1 (CH_2), 21.9 (CH_2), 22.0 (CH_2), 19.7 (CH_2). mp 132°C. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97, H, 6.99, N, 7.48. Found : C, 76.30, H, 7.09, N, 7.18. Sensitive to air and turn black rapidly.

6-Ethylthio-1,2,3,4-Tetrahydrocarbazole **3b, R^1R^2=$(CH_2)_4$, R^3=H, R^4=Et**

IR (NaCl) 3408 (NH), 2925-2840 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.7-6.8 (4 H, m, AromH+NH), 3.1-2.3 (6 H, m+q, SCH_2+2xCH_2), 2.2-1.5 (4 H, m, 2xCH_2), 1.5-1.0 (3 H, t, Me). ^{13}C NMR ($CDCl_3$) δ ppm : 134.9 (Arom CS), 134.8 (Arom C), 128.4 (Arom C), 125.5 (Arom CH), 124.2 (Arom C), 122.1 (Arom CH), 110.6 (Arom CH), 109.8 (Arom C), 30.5 (SCH_2), 23.08 (2xCH_2), 23.01 (CH_2), 20.72 (CH_2), 14.70 ($SCH_2\underline{C}H_3$). mp 60°C. Anal. Calcd for $C_{14}H_{17}NS$: C, 72.67, H, 7.40, N, 6.05, S, 13.85. Found : C, 72.40, H, 7.54, N, 6.15, S, 13.59.

1,2,3,4-Tetrahydro-6-hydroxy-9-methylcarbazole **2c, R^1R^2=$(CH_2)_5$, R^3=Me**

IR (NaCl) 3349 (OH), 2920-2845 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 6.5-7.3 (3 H, m, Arom H), 5.2 (1 H, s, OH), 3.6 (3 H, s, NMe), 2.5-3.0 (4 H, m, 2xCH_2), 1.5-2.0 (6 H, m, 3xCH_2). ^{13}C NMR ($CDCl_3$) δ ppm : 148.8 (Arom COH), 140.0 (Arom C), 131.3 (Arom C), 128.1 (Arom C), 112.6 (Arom C), 109.7 (Arom CH), 109.2 (Arom CH), 102.4 (Arom CH), 31.4 (CH_2), 29.4 (NMe), 28.3 (CH_2), 26.9 (CH_2), 26.2 (CH_2), 24.3 (CH_2). mp 102°C. Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10, H, 7.96, N, 6.50. Found : C, 77.69, H, 7.85, N, 6.52.

3-Ethylthio-10-methyl-5,6,7,8,9,10-hexahydrocyclohept[b]indole **3c, R^1R^2=$(CH_2)_5$, R^3=Me, R^4=Et**

IR (NaCl) 2921-2846 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.60 (s,1 H, Arom H), 7.25-7.10 (m, 2 H, Arom H), 3.60 (s, 3 H, NMe), 2.90-2.70 (m+q, 6 H, SCH_2+2xCH_2), 1.95-1.70 (m, 6 H, 3xCH_2), 1.30-1.15 (t, 3 H, Me). ^{13}C NMR ($CDCl_3$) δ ppm : 139.8 (Arom CS), 135.1 (Arom C), 128.2 (Arom C), 125.1 (Arom CH), 123.7 (Arom C), 122.3 (Arom CH), 111.3 (Arom C), 109.1 (Arom CH), 31.4 (CH_2), 30.8 (SCH_2), 28.3 (CH_2), 26.9 (CH_2), 26.2 (CH_2), 24.2 (CH_2), 29.5 (NMe), 14.8 ($SCH_2\underline{C}H_3$). mp 44°C. Anal. Calcd for $C_{16}H_{21}NS$: C, 74.07, H, 8.16, N, 5.39, S, 12.36. Found : C, 74.04, H, 8.16, N, 5.36, S, 12.40.

5,6,7,8,9,10-Hexahydro-3-hydroxy-cyclohept[b]indole **2d, R^1R^2=$(CH_2)_5$, R^3=H**

IR (NaCl) 3420 (OH), 3267 (NH), 2929 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 8.3 (1 H, s, OH), 7.3-6.3 (4 H, m, Arom H+NH), 3.0-2.5 (4 H, m, 2xCH_2), 2.2-1.5 (6 H, m, 3xCH_2). ^{13}C NMR ($CDCl_3$) δ ppm : 149.8 (Arom COH), 138.4 (Arom C), 129.5 (Arom C), 128.8 (Arom C), 112.2 (Arom C), 110.4 (Arom CH), 109.8 (Arom CH), 101.9 (Arom CH), 31.5 (CH_2), 29.1 (CH_2), 28.5 (CH_2), 27.2 (CH_2), 24.4 (CH_2). mp 174°C. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.55, H, 7.51, N, 6.95. Found : C, 77.28, H, 7.54, N, 7.09.

3-Ethylthio-5,6,7,8,9,10-hexahydro-cyclohept[b]indole **3d, R^1R^2=$(CH_2)_5$, R^3=H, R^4=Et**

IR (NaCl) 3409 (NH), 2923-2848-2694 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.5-6.7 (4 H, m, Arom H+NH), 3.0-2.3 (6 H, q+m, SCH_2+2xCH_2), 2.0-1.4 (6 H, m, 3xCH_2), 1.4-1.0 (3 H, t, Me). ^{13}C NMR ($CDCl_3$) δ ppm : 138.2 (Arom CS), 133.2 (Arom C), 129.6 (Arom C), 124.9 (Arom CH), 123.9 (Arom C), 121.9 (Arom CH), 113.1 (Arom C), 110.5 (Arom CH), 31.5 (CH_2), 30.4 (SCH_2), 29.2 (CH_2), 28.4 (CH_2), 27.1 (CH_2), 24.3 (CH_2), 14.7 ($SCH_2\underline{C}H_3$). mp 63°C. Anal. Calcd for $C_{15}H_{19}NS$: C, 73.41, H, 7.80, N, 5.70, S, 13.06. Found : C, 73.76, H, 7.82, N, 5.70, S, 13.30.

5,6,7,8,9,10,11-Heptahydro-3-hydroxy-11-methylcyclooct[b]indole **2e, R^1R^2=$(CH_2)_6$, R^3=Me**

IR (NaCl) 3368 (OH), 2925-2847 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.00-6.35 (3 H, m, Arom H), 5.55 (1 H, s, OH), 3.50 (3 H, s, NMe), 3.00-2.50 (4 H, m, 2xCH_2), 1.90-1.00 (8 H, m, 4xCH_2). ^{13}C NMR ($CDCl_3$) δ ppm : 148.7 (Arom COH), 138.0 (Arom C), 132.0 (Arom C), 127.7 (Arom C), 110.8 (Arom C), 109.5 (Arom CH), 109.0 (Arom CH), 102.4 (Arom CH), 30.4 (CH_2), 29.2 (NMe), 28.6 (CH_2), 25.8 (2xCH_2), 22.9

($2xCH_2$). mp 98°C. Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56, H, 8.35, N, 6.12. Found : C, 78.07, H, 8.30, N, 6.12.

3-Ethylthio-5,6,7,8,9,10,11-heptahydro-11-methylcyclooct[b]indole **3e, R^1R^2=$(CH_2)_6$, R^3=Me, R^4=Et**
IR (NaCl) 2926-2850 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.60 (1 H, s, Arom H), 7.30-7.00 (2 H, m, Arom H), 3.51 (3 H, s, NMe), 2.95-2.70 (6 H, m+q, SCH_2+$2xCH_2$), 1.75-1.50 (4 H, m, $2xCH_2$), 1.40-1.10 (7 H, m+t, $2xCH_2$+Me). ^{13}C NMR ($CDCl_3$) δ ppm : 137.5 (Arom CS), 135.6 (Arom C), 127.7 (Arom C), 124.7 (Arom CH), 123.5 (Arom C), 121.9 (Arom CH), 111.1 (Arom C), 108.8 (Arom CH), 30.6 (SCH_2), 30.3 (CH_2), 28.4 (CH_2), 25.6 ($2xCH_2$), 22.7 ($2xCH_2$), 29.0 (NMe), 14.6 ($SCH_2\underline{C}H_3$). Anal. Calcd for $C_{17}H_{23}NS$: C, 74.67, H, 8.47, N, 5.12. Found : C, 74.51, H, 8.37, N, 5.21.

5,6,7,8,9,10,11-Heptahydro-3-hydroxycyclooct[b]indole **2f, R^1R^2=$(CH_2)_6$, R^3=H**
IR (NaCl) 3404 (OH+NH), 2922-2849 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.25 (1 H, s, NH), 6.90-6.25 (3 H, m, Arom H), 5.45 (1 H, s, OH), 2.70-2.25 (4 H, m, $2xCH_2$), 1.90-1.00 (8 H, m, $4xCH_2$). ^{13}C NMR ($CDCl_3$) δ ppm : 148.8 (Arom COH), 137.0 (Arom C), 130.2 (Arom C), 129.2 (Arom C), 111.0 (Arom C), 110.8 (Arom CH), 109.9 (Arom CH), 102.5 (Arom CH), 29.4 (CH_2), 29.3 (CH_2), 25.9 (CH_2), 25.7 (CH_2), 25.7 (CH_2), 22.0 (CH_2). mp 92°C. Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10, H, 7.96, N, 6.50. Found : C, 77.67, H, 7.94, N, 6.58.

3-Ethylthio-5,6,7,8,9,10,11-heptahydrocyclooct[b]indole **3f, R^1R^2=$(CH_2)_6$, R^3=H, R^4=Et**
IR (NaCl) 3403 (NH), 2923-2848 (C-H). ^1H NMR (CCl_4) δ ppm : 7.5-6.7 (4 H, m, Arom H+NH), 3.0-2.4 (6 H, m+q, SCH_2+$2xCH_2$), 2.0-1.0 (11 H, m+t, $4xCH_2$+Me). ^{13}C NMR ($CDCl_3$) δ ppm 136.4 (Arom CS), 134.2 (Arom C), 129.2 (Arom C), 125.1 (Arom CH), 124.2 (Arom C), 122.0 (Arom CH), 111.4 (Arom C), 110.6 (Arom CH), 30.5 (SCH_2), 29.4 (CH_2), 29.3 (CH_2), 25.9 (CH_2), 25.7 (CH_2), 22.0 ($2xCH_2$), 14.7 ($SCH_2\underline{C}H_3$). mp 54°C. Anal. Calcd for $C_{16}H_{21}NS$: C, 74.07, H, 8.16, N, 5.39. Found : C, 74.24, H, 8.19, N, 5.16.

5,6,7,8,9,10,11,12,13,14,15-Undecahydro-3-hydroxy-15-methylcyclododec[b]indole **2g, R^1R^2=$(CH_2)_{10}$, R^3=Me**
IR (NaCl) 3340 (OH), 2931-2849 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.20-6.50 (3 H, m, Arom H), 4.50 (1 H, s, OH), 3.52 (3 H, s, NMe), 2.90-2.30 (4 H, m, $2xCH_2$), 2.00-0.90 (16 H, m, $8xCH_2$). ^{13}C NMR ($CDCl_3$) δ ppm : 148.6 (Arom COH), 138.2 (Arom C), 132.4 (Arom C), 128.2 (Arom C), 111.2 (Arom C), 109.9 (Arom CH), 108.8 (Arom CH), 103.6 (Arom CH), 29.8 (NMe), 27.7 (CH_2), 27.2 (CH_2), 25.2 (CH_2), 24.9 (CH_2), 24.5 (CH_2), 24.4 (CH_2), 22.2 (CH_2), 22.1 (CH_2), 21.6 (CH_2), 21.5 (CH_2). mp 120°C. Anal. Calcd for $C_{19}H_{27}NO$: C, 79.94, H, 9.53, N, 4.90. Found : C, 80.21, H, 9.63, N, 4.81.

3-Ethylthio-5,6,7,8,9,10,11,12,13,14,15-Undecahydro-15-methylcyclododec[b]indole **3g, R^1R^2=$(CH_2)_{10}$, R^3=Me, R^4=Et**
IR (NaCl) 2927-2850 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.7-6.8 (3 H, m, Arom H), 3.4 (3 H, s, NMe), 3.0-2.3 (6 H, m+q, SCH_2+$2xCH_2$), 2.0-1.7 (19 H, m, $8xCH_2$+Me). ^{13}C NMR ($CDCl_3$) δ ppm : 37.7 (Arom CS), 136.2 (Arom C), 128.3 (Arom C), 125.4 (Arom CH), 123.6 (Arom C), 123.4 (Arom CH), 111.8 (Arom C), 108.7 (Arom CH), 30.7 (SCH_2), 28.0 (CH_2), 27.2 (CH_2), 25.1 (CH_2), 24.9 (CH_2), 24.6 (CH_2), 24.4 (CH_2), 22.1 ($2xCH_2$), 21.6 (CH_2), 21.4 (CH_2), 14.7 ($SCH_2\underline{C}H_3$). mp 55°C. X-ray diffraction data were collected and published.[9]

5,6,7,8,9,10,11,12,13,14,15-Undecahydrocyclododec[b]indole **2h, R^1R^2=$(CH_2)_{10}$, R^3=H**
IR (NaCl) 3609 (OH), 3408 (NH), 3028-2934-2852 (C-H). ^1H NMR ($CDCl_3$) δ ppm : 7.3 (s, 1 H, NH), 7.0-6.3 (m, 3 H, Arom H), 5.3 (s, 1 H, OH), 2.9-2.3 (m, 4 H, $2xCH_2$), 2.0-0.8 (m, 16 H, $8xCH_2$). ^{13}C NMR ($CDCl_3$) δ ppm : 148.4 (Arom COH), 137.0 (Arom C), 130.8 (Arom C), 129.0 (Arom C),111.3 (Arom C), 110.6 (Arom CH), 110.1 (Arom CH), 103.6 (Arom CH), 27.2 (CH_2), 27.1 (CH_2), 24.6 ($2xCH_2$), 24.5 (CH_2), 23.8 (CH_2), 22.3 ($2xCH_2$), 21.9 (CH_2), 20.9 (CH_2). mp 45°C. Anal. Calcd for $C_{18}H_{25}NO$: C, 79.65. H, 9.28, N, 5.16, O, 5.91. Found : C, 79.08, H, 9.48, N, 5.17, O, 6.22. Sensitive to air and turn black rapidly.

3-Ethylthio-5,6,7,8,9,10,11,12,13,14,15-undecahydrocyclododec[b]indole **3h, $R^1R^2=(CH_2)_{10}$, R^3=H, R^4=Et**

IR (NaCl) 3412 (NH), 2974-2933-2852 (C-H). ^{1}H NMR ($CDCl_3$) δ ppm : 7.7-6.7 (4 H, m, Arom H+NH), 3.0-2.4 (6 H, m+q, SCH_2+2xCH_2), 2.0-0.8 (19 H, m, 8xCH_2+Me). ^{13}C NMR ($CDCl_3$) δ ppm : 136.6 (Arom CS), 135.0 (Arom C), 129.2 (Arom C), 125.7 (Arom CH), 124.1 (Arom C), 123.3 (Arom CH), 112.2 (Arom C), 110.5 (Arom CH), 30.7 (SCH_2), 27.6 (CH_2), 27.2 (CH_2), 24.8 (2xCH_2), 23.9 (CH_2), 22.5 (2xCH_2), 22.1 (2xCH_2), 21.1 (CH_2), 14.76 ($SCH_2\underline{C}H_3$). mp 100°C. Anal. Calcd for $C_{20}H_{29}NS$: C, 76.13, H, 9.26, N, 4.43, S, 10.16. Found : C, 75.91, H, 9.25, N, 4.32, S, 10.02.

5-Hydroxy-1,2-dimethylindole **2i, R^1=H, R^2=Me, R^3=Me**

IR (NaCl) 3191 (OH). ^{1}H NMR ($CDCl_3$) δ ppm : 7.25-6.47 (3 H, m, Arom H), 6.03 (1 H, s, Arom H), 4.36 (1 H, s, OH), 3.56 (3 H, s, NMe), 2.36 (3 H, s, Me). ^{13}C NMR ($CDCl_3$) δ ppm : 149.2 (Arom COH), 137.7 (Arom C), 132.7 (Arom C), 128.4 (Arom C), 109.7 (Arom CH), 109.1 (Arom CH), 104.3 (Arom CH), 98.7 (Arom CH), 29.3 (NMe), 12.7 (Me). mp 143°C. Anal. Calcd for $C_{10}H_{11}NO$: C, 74.50, H, 6.87, N, 8.68. Found : C, 74.34, H, 6.79, N, 8.49.

5-Hydroxy-1-methyl-2-thienylindole **2j, R^1=H, R^2=2-Thienyl, R^3=Me**

IR (NaCl) 3365 (OH), 2942 (C-H). ^{1}H NMR ($CDCl_3$) δ ppm : 7.5-6.4 (7 H, m, Arom H), 4.7 (1 H, s, OH), 3.7 (3 H, s, NMe). ^{13}C NMR ($CDCl_3$/DMSO) δ ppm : 150.11 (Arom COH), 132.85 (Arom C), 132.81 (Arom C), 132.01 (Arom C), 126.94 (Arom C), 126.52 (2xArom CH), 125.00 (2xArom CH), 111.23 (Arom CH), 108.88 (Arom CH), 103.10 (Arom CH), 100.21 (Arom CH), 29.83 (NMe). mp 117°C. Anal. Calcd for $C_{13}H_{11}NOS$: C, 68.09, H, 4.83, N, 6.10, S, 13.98. Found : C, 67.91, H, 4.81, N, 6.19, S, 13.75.

5-Ethylthio-3-pentylindole **3k, R^1=*n*-C_5H_{11}, R^2=H, R^3=H, R^4=Et**

IR (NaCl) 3422 (NH), 2957-2927-2855 (C-H). ^{1}H NMR ($CDCl_3$) δ ppm : 7.7-6.6 (5 H, m, Arom H+NH), 3.1-2.5 (4 H, m+q, SCH_2+CH_2), 1.9-0.6 (12 H, m+t, $SCH_2\underline{C}H_3$+3xCH_2+CH_3). ^{13}C NMR ($CDCl_3$) δ ppm : 135.5 (Arom CS), 128.2 (Arom C), 126.2 (Arom CH), 124.4 (Arom C), 123.2 (Arom CH), 121.7 (Arom CH), 116.8 (Arom C), 111.4 (Arom CH), 31.7 (SCH_2), 30.4 (CH_2), 29.7 (CH_2), 24.8 (CH_2), 22.4 (CH_2), 14.6 ($SCH_2\underline{C}H_3$), 13.9 (Me). Anal. Calcd for $C_{15}H_{21}NS$: C, 72.81, H, 8.55, N, 5.66. Found : C, 72.86, H, 8.55, N, 5.67.

N-Phenyl-2-(5-hydroxymethylindole) carboxamide **5a, R^1=Me, R^2=Ph, R^3=H**

IR (NaCl) 3284 (OH+NH), 1645 (CO). ^{1}H NMR ($CDCl_3$/DMSO) δ ppm : 10.0 (1 H, s, NH), 8.6 (1 H, s, OH), 7.9-6.7 (9 H, m, Arom H), 4.0 (3 H, s, NMe). ^{13}C NMR ($CDCl_3$/DMSO) δ ppm : 159.9 (CO), 150.4 (Arom COH), 137.8 (Arom C), 133.0 (Arom C), 131.3 (Arom C), 127.5 (2xArom CH), 122.6 (Arom CH), 119.4 (2xArom CH), 125.4 (Arom C), 114.1 (Arom CH), 109.5 (Arom CH), 104.0 (Arom CH), 103.5 (Arom CH), 30.5 (NMe). mp 195°C. Anal. Calcd for $C_{16}H_{14}O_2N_2$: C, 72.16, H, 5.29, N, 10.52. Found : C, 71.67, H, 5.31, N, 10.13.

N-Phenyl-2-(5-ethylthiomethylindole) carboxamide **6a, R^1=Me, R^2=Ph, R^3=H, R^4=Et**

IR (NaCl) 3294 (NH), 2927 (C-H), 1646(CO). ^{1}H NMR ($CDCl_3$) δ ppm : 8.0-6.8 (10 H, m, Arom H+NH), 4.0 (3 H, s, NMe), 3.1-2.7 (2 H, q, SCH_2), 1.4-1.1 (3 H, t, $SCH_2\underline{C}H_3$). ^{13}C NMR ($CDCl_3$) δ ppm : 160.6 (CO), 138.2 (Arom CS), 137.6 (Arom C), 132.4 (Arom C), 128.9 (2xArom CH), 124.9 (Arom CH), 120.0 (2xArom CH), 128.2 (Arom CH), 124.3 (Arom CH), 126.6 (Arom C), 126.3 (Arom C), 110.5 (Arom CH), 103.9 (Arom CH), 31.5 (NMe), 29.7 (SCH_2), 14.4 ($SCH_2\underline{C}H_3$). mp 130°C. Anal. Calcd for $C_{18}H_{18}ON_2S$: C, 69.64, H, 5.84, N, 9.02, S, 10.32. Found : C, 69.48, H, 5.99, N, 8.81, S, 10.22.

N-Phenyl-2-(methylindole) carboxamide **7a, R^1=Me, R^2=Ph, R^3=H**

IR (NaCl) 3283 (NH), 1643 (C=O). ^{1}H NMR ($CDCl_3$) δ ppm : 7.9 (1 H, s, NH),7.9-6.7 (10 H, m, Arom H), 4.0 (3 H, s, NMe). ^{13}C NMR ($CDCl_3$) δ ppm : 160.5 (CO), 139.2 (Arom C), 137.6 (Arom C), 131.9 (Arom C),129.1 (2xArom CH), 125.8 (Arom C), 124.6 (Arom CH), 124.4 (Arom CH), 121.9 (Arom CH), 120.6 (Arom CH), 120.0 (2xArom CH), 110.1 (Arom CH), 104.2 (Arom CH), 31.5 (NMe). mp 147°C. Anal. Calcd for $C_{16}H_{14}ON_2$: C, 76.77, H, 5.63, N, 11.19. Found : C, 76.64, H, 5.73, N, 10.99.

N-Methyl-N-phenyl-2-(5-hydroxyindole) carboxamide **5b, R^1=H, R^2=Ph, R^3=Me**

IR (NaCl) 3306 (OH, NH), 1611 (C=O). ^{1}H NMR ($CDCl_3$/DMSO) δ ppm : 10.0 (1 H, s, NH), 7.7-6.7 (9 H, m, Arom H+OH), 5.2 (1 H, s, Arom H2), 3.4 (3 H, s, NMe). ^{13}C NMR ($CDCl_3$/DMSO) δ ppm : 160.7 (CO), 149.7 (Arom COH), 143.1 (Arom C), 129.3 (Arom C), 128.8 (Arom C), 128.3 (2xArom CH), 126.6 (Arom CH), 126.4 (2xArom CH), 126.1 (Arom C), 113.8 (Arom CH), 111.3 (Arom CH), 104.1 (Arom CH), 103.2 (Arom CH), 37.4 (NMe). mp 193°C. Anal. Calcd for $C_{16}H_{14}O_2N_2$: C, 72.16, H, 5.29, N, 10.52. Found : C, 71.86, H, 5.16, N, 10.24.

N-Methyl-N-phenyl-2-(5-ethylthioindole) carboxamide **6b, R^1=H, R^2=Ph, R^3=Me, R^4=Et**

IR (NaCl) 3269 (NH), 2962-2925 (C-H), 1621 (C=O). ^{1}H NMR ($CDCl_3$) δ ppm : 10.1 (1 H, s, NH), 7.7-7.0 (8 H, m, Arom H), 5.2 (1 H, s, Arom H2), 3.5 (3 H, s, NMe), 3.5-3.1 (2 H, q, SCH_2), 2.5-1.5 (3 H, t, $SCH_2\underline{CH_3}$). ^{13}C NMR ($CDCl_3$) δ ppm : 161.9 (CO), 143.9 (Arom CS), 134.5 (Arom C), 130.1 (Arom C), 129.9 (2xArom CH), 127.9 (3xArom CH), 128.5 (Arom CH), 128.2 (Arom C), 126.0 (Arom C), 125.5 (Arom CH), 112.0 (Arom CH), 106.5 (Arom CH), 38.9 (NMe), 29.8 (SCH_2), 14.5 ($SCH_2\underline{CH_3}$). mp 169°C. Anal. Calcd for $C_{18}H_{18}ON_2S$: C, 69.64, H, 5.84, N, 9.02, S, 10.32. Found : C, 69.36, H, 6.16, N, 9.28, S, 9.83.

N-Methyl-N-phenyl-2-indolecarboxamide **7b, R^1=H, R^2=Ph, R^3=Me**

IR (NaCl) 3275 (NH), 3060-2925 (C-H), 1618 (C=O). ^{1}H NMR ($CDCl_3$) δ ppm : 10.3-9.9 (1 H, s, NH), 7.5-6.6 (9 H, m, Arom H), 5.2 (1 H, s, Arom H2), 3.5 (3 H, s, NMe). ^{13}C NMR ($CDCl_3$) δ ppm : 162.1 (CO), 144.0 (2xArom C), 135.4 (Arom C), 129.8 (2xArom CH), 128.3 (Arom CH), 127.9 (2xArom CH), 127.5 (Arom C), 124.2 (Arom CH), 122.0 (Arom CH), 120.0 (Arom CH), 111.6 (Arom CH), 107.0 (Arom CH), 38.9 (NMe). mp 173°C. Anal. Calcd for $C_{16}H_{14}ON_2$: C, 76.77, H, 5.63, N, 11.19. Found : C, 76.43, H, 5.68, N, 11.03.

N-Methyl-N-phenyl-2-[(5-hydroxy)methylindole] carboxamide **5c, R^1=Me, R^2=Ph, R^3=Me**

IR (NaCl) 3850 (OH), 2926 (C-H), 1619 (CO). ^{1}H NMR ($CDCl_3$) δ ppm : 6.60-7.50 (8 H, m, Arom H), 5.85 (1 H, s, OH), 5.00 (1 H, s, Arom H2), 3.90 (3 H, s, NMe), 3.50 (3 H, s, NMe). ^{13}C NMR ($CDCl_3$) δ ppm : 164.0 (CO), 150.1 (Arom COH), 144.5 (Arom C), 133.1 (Arom C), 132.0 (2xArom C), 129.2 (2xArom CH), 126.9 (Arom CH), 126.4 (Arom CH), 125.3 (Arom CH), 114.2 (Arom CH), 110.2 (Arom CH), 106.5 (Arom CH), 105.3 (Arom H), 38.2 (NMe), 31.4 (NMe). mp 139°C. Anal. Calcd for $C_{17}H_{16}O_2N_2$: C, 72.83, H, 5.75, N, 9.99. Found : C, 72.99, H, 5.79, N, 9.96.

N-Methyl-N-phenyl-2-(methylindole) carboxamide **7c, R^1=Me, R^2=Ph, R^3=Me**

IR (NaCl) 2938 (C-H), 1638 (CO). ^{1}H NMR ($CDCl_3$) δ ppm : 7.5-6.8 (9 H, m, Arom H), 6.0 (1 H, s, Arom H2), 3.9 (3 H, s, NMe), 3.4 (3 H, s, NMe). ^{13}C NMR ($CDCl_3$) δ ppm : 163.3 (CO), 144.5 (Arom C), 137.4 (Arom C), 131.7 (Arom C), 128.9 (2xArom CH), 126.5 (Arom CH), 126.2 (2xArom CH), 125.8 (Arom C), 123.1 (Arom CH), 121.4 (Arom CH), 119.6 (Arom CH), 109.4 (Arom CH), 106.9 (Arom CH), 37.8 (NMe), 31.2 (NMe). mp 84°C. Anal. Calcd for $C_{17}H_{16}ON_2$: C, 77.24, H, 6.10, N, 10.60, O, 6.05. Found : C, 77.18, H, 6.22, N, 10.48, O, 6.05.

N-Butyl-N-phenyl-2-(5-hydroxyindole) carboxamide **5d, R^1=H, R^2=Ph, R^3=*n*-C_4H_9**

IR (NaCl) 3309 (NH, OH), 2959 (C-H), 1609 (CO). ^{1}H NMR ($CDCl_3$/DMSO) δ ppm : 9.85 (1 H, s, NH), 7.90 (1 H, s, OH), 7.40-6.40 (8 H, m, Arom H), 4.90 (1 H, s, Arom H2), 4.00-3.50 (2 H, m, NCH_2), 1.90-0.70 (7 H, m, $2xCH_2$ +CH_3). ^{13}C NMR ($CDCl_3$/DMSO) δ ppm : 160.7 (CO), 150.1 (Arom COH), 141.9 (Arom C), 129.7 (Arom C), 129.4 (Arom C), 128.7 (2xArom CH), 127.8 (Arom CH), 127.3 (2xArom CH), 127.1 (Arom C), 114.3 (Arom CH), 111.5 (Arom CH), 104.7 (Arom CH), 103.8 (Arom CH), 49.5 (NCH_2), 28.7 (CH_2), 19.1 (CH_2), 13.0 (CH_3). mp 157°C. Anal. Calcd for $C_{19}H_{20}O_2N_2$: C, 73.99, H, 6.53, N, 9.08. Found : C, 73.75, H, 6.51, N, 8.91.

N-Butyl-N-phenyl-2-(5-ethylthioindole) carboxamide **6d, R^1=H, R^2=Ph, R^3=*n*-C_4H_9, R^4=Et**

IR (NaCl) 3281 (NH), 3256-2930-2862 (C-H), 1612 (CO). ^{1}H NMR ($CDCl_3$) δ ppm : 10.25 (1 H, s, NH), 7.70-7.00 (8 H, m, Arom H), 5.10 (1 H, s, Arom H2), 4.20-3.70 (2 H, m, NCH_2), 3.00-2.50 (2 H, q, SCH_2), 2.00-0.70 (10 H, m+t, $2xCH_2$+CH_3+$SCH_2\underline{CH_3}$). ^{13}C NMR ($CDCl_3$) δ ppm : 161.4 (CO), 142.5 (Arom CS), 134.5 (Arom C), 130.3 (Arom C), 129.7 (2xArom CH), 128.8 (Arom CH), 128.5 (2xArom CH), 128.4 (Arom

CH), 128.2 (Arom C), 125.9 (Arom C), 125.5 (Arom CH), 112.0 (Arom CH), 106.3 (Arom CH), 50.8 (NCH_2), 29.9 (SCH_2), 29.6 (CH_2), 20.1 (CH_2), 14.5 ($SCH_2\underline{C}H_3$), 13.8 (CH_3). mp 142°C. Anal. Calcd for $C_{21}H_{24}ON_2S$: C, 71.55, H, 6.86, N, 7.94, S, 9.09. Found : C, 71.77, H, 7.01, N, 7.95, S, 8.83.

N-Butyl-N-phenyl-2-indolecarboxamide **7d, R^1=H, R^2=Ph, R^3=*n*-C_4H_9**

IR (NaCl) 3285 (NH), 1613 (CO). ^1H NMR ($CDCl_3$) δ ppm : 10.4 (1 H, s, NH), 7.6-6.7 (9 H, m, Arom H), 5.1 (1 H, s, Arom H2), 4.1-3.7 (2 H, m, NCH_2), 2.0-0.7 (7 H, m, $2xCH_2$+CH_3). ^{13}C NMR ($CDCl_3$) δ ppm : 161.8 (CO), 142.7 (Arom C), 135.6 (Arom C), 135.5 (Arom C), 127.5 (Arom C), 129.6 (2xArom CH), 128.8 (Arom CH), 128.3 (2xArom CH), 124.0 (Arom CH), 121.9 (Arom CH), 119.8 (Arom CH), 111.7 (Arom CH), 106.8 (Arom CH), 50.87 (NCH_2), 29.60 (CH_2), 20.11 (CH_2), 13.78 (CH_3). mp 147°C. Anal. Calcd for $C_{19}H_{20}ON_2$: C, 78.04, H, 6.89, N, 9.58. Found : C, 77.91, H, 7.10, N, 9.61.

N-Butyl-N-phenyl-2-(5-hydroxymethylindole) carboxamide **5e, R^1=Me, R^2=Ph, R^3=*n*-C_4H_9**

IR (NaCl) 3373 (OH), 2959-2871 (C-H), 1614 (CO). ^1H NMR ($CDCl_3$) δ ppm : 7.4-6.5 (9 H, m, Arom H+OH), 5.7 (1 H, s, Arom H2), 4.0-3.7 (2 H, m, NCH_2), 3.7 (3 H, s, NMe), 1.9-1.1 (4 H, m, $2xCH_2$), 1.1-0.7 (3 H, m, CH_3). ^{13}C NMR ($CDCl_3$) δ ppm : 163.7 (CO), 149.9 (Arom COH), 143.1 (Arom C), 133.0 (Arom C), 132.6 (Arom C), 129.1 (2xArom CH), 127.3 (Arom CH), 127.0 (2xArom CH), 126.5 (Arom C), 114.0 (Arom CH), 110.1 (Arom CH), 106.0 (Arom CH), 105.4 (Arom CH), 50.2 (NCH_2), 31.4 (NMe), 29.7 (CH_2), 20.0 (CH_2), 13.7 (CH_3). mp 150°C. Anal. Calcd for $C_{20}H_{22}O_2N_2$: C, 74.50, H, 6.87, N, 8.69. Found : C, 74.45, H, 7.18, N, 8.49.

N-Butyl-N-phenyl-2-[(5-ethylthio)methylindole] carboxamide **6e, R^1=Me, R^2=Ph, R^3=*n*-C_4H_9, R^4=Et**

IR (NaCl) 3060-2959-2871 (C-H), 1638 (CO). ^1H NMR ($CDCl_3$) δ ppm : 7.5-6.7 (8 H, m, Arom H), 5.7 (1 H, s, Arom H2), 3.9 (3 H, s, NMe), 4.2-3.7 (2 H, m, NCH_2), 3.0-2.5 (2 H, q, SCH_2), 1.9-0.7 (10 H, m+t, $2xCH_2$+ CH_3+$SCH_2\underline{C}H_3$). ^{13}C NMR ($CDCl_3$) δ ppm : 162.7 (CO), 143.1 (Arom CS), 136.6 (Arom C), 132.9 (Arom C), 129.0 (2xArom CH), 127.2 (3xArom CH), 126.8 (Arom CH), 126.5 (Arom C), 125.6 (Arom C), 124.9 (Arom CH), 109.9 (Arom CH), 106.1 (Arom CH), 49.8 (NCH_2), 31.4 (NMe), 29.7 (CH_2), 29.6 (SCH_2), 19.9 (CH_2), 14.4 ($SCH_2\underline{C}H_3$), 13.6 (CH_3). Anal. Calcd for $C_{22}H_{26}ON_2S$: C, 72.09, H, 7.15, N, 7.64, S, 8.74. Found : C, 72.29, H, 7.48, N, 7.52, S, 8.62.

N-Butyl-N-phenyl-2-methylindolecarboxamide **7e, R^1=Me, R^2=Ph, R^3=*n*-C_4H_9**

IR (NaCl) 2957-2932 (C-H), 1642 (CO). ^1H NMR (CCl_4) δ ppm : 7.40-6.60 (9 H, m, Arom H), 5.70 (1 H, s, Arom H2), 4.00-3.60 (2 H, m, NCH_2), 3.85 (3 H, s, NMe), 1.90-0.70 (7 H, m, $2xCH_2$+CH_3). ^{13}C NMR ($CDCl_3$) δ ppm : 162.2 (CO), 143.4 (Arom C), 137.6 (Arom C), 132.4 (Arom C), 129.1 (2xArom CH), 127.4 (Arom CH), 126.9 (2xArom CH), 126.1 (Arom C), 123.2 (Arom CH), 121.7 (Arom CH), 119.7 (Arom CH), 109.6 (Arom CH), 106.8 (Arom CH), 31.4 (NMe), 29.7 (NCH_2), 20.1 (CH_2), 20.0 (CH_2), 13.7 (CH_3). Anal. Calcd for $C_{20}H_{22}ON_2$: C, 78.39, H, 7.24, N, 9.14. Found : C, 78.57, H, 7.32, N, 9.06.

N-Hexyl-N-phenyl-2-(5-hydroxyindole) carboxamide **5f, R^1=H, R^2=Ph, R^3=*n*-C_6H_{13}**

IR (NaCl/nujol) 3420 (OH), 3269 (NH), 1613 (CO). ^1H NMR ($CDCl_3$/DMSO) δ ppm : 9.26 (1 H, s, NH), 7.56-6.65 (8 H, m, Arom H), 5.00 (1 H, s, Arom H2), 4.84 (1 H, s, OH), 4.00-3.78 (2 H, m, NCH_2), 1.75-0.75 (11 H, m, $4xCH_2$+CH_3). ^{13}C NMR ($CDCl_3$/DMSO) δ ppm : 160.3 (CO), 149.8 (Arom COH), 141.7 (Arom C), 129.4 (Arom C), 129.2 (Arom C), 128.4 (2xArom CH), 127.5 (2xArom CH), 126.9 (Arom CH), 126.7 (Arom C), 113.9 (Arom CH), 111.3 (Arom CH), 104.2 (Arom CH), 103.4 (Arom CH), 49.3 (NCH_2), 30.2 (CH_2), 26.2 (CH_2), 25.2 (CH_2), 21.2 (CH_2), 12.8 (CH_3). mp 164°C. Anal. Calcd for $C_{21}H_{24}O_2N_2$: C, 74.96, H, 7.19, N, 8.32. Found : C, 74.70, H, 7.27, N, 8.27.

N-Hexyl-N-phenyl-2-(5-ethylthioindole) carboxamide **6f, R^1=H, R^2=Ph, R^3=*n*-C_6H_{13}, R^4=Et**

IR (NaCl) 3275 (NH), 2960-2927-2855 (C-H), 1613 (CO). ^1H NMR ($CDCl_3$) δ ppm : 10.80 (1 H, s, NH), 7.60-6.90 (8 H, m, Arom H), 5.05 (1 H, s, Arom H2), 4.10-3.60 (2 H, m, NCH_2), 3.00-2.50 (2 H, q, SCH_2), 2.10-0.60 (14 H, m+t, $4xCH_2$+CH_3+$SCH_2\underline{C}H_3$). ^{13}C NMR ($CDCl_3$) δ ppm : 161.5 (CO), 142.6 (Arom CS), 134.6 (Arom C), 130.3 (Arom C), 129.8 (Arom CH), 128.9 (3xArom CH), 128.5 (2xArom CH), 128.3 (Arom C), 126.0 (Arom C), 125.5 (Arom CH), 112.1 (Arom CH), 106.4 (Arom CH), 51.1 (NCH_2), 31.5 (CH_2), 29.9

(SCH_2), 27.5 (CH_2), 26.5 (CH_2), 22.5 (CH_2), 14.6 (SCH_2), 13.9 (CH_3). mp 112°C. Anal. Calcd for $C_{23}H_{28}ON_2S$: C, 72.59, H, 7.41, N, 7.36, S, 8.42. Found : C, 72.34, H, 7.49, N, 7.43, S, 8.02. X-Ray diffraction data have been collected : monoclinic space group $P2_1/c$, a=13.184(2), b=9.077(2), c=17.750(4) Å ; β=91.98(1), Cu-Kα (λ=1;54178 Å). The structure has been solved by direct methods and refined on F^2 down to R(F)=0.0696 on 1318 Fo > 4σ (Fo) observed reflections. A complete report on this structure is going to be published elsewhere.

N-Hexyl-N-phenyl-2-indolecarboxamide **7f, R^1=H, R^2=Ph, R^3=*n*-C_6H_{13}**

IR (NaCl) 3274 (NH), 2957-2928-2853 (C-H), 1614 (CO). ^1H NMR ($CDCl_3$) δ ppm : 10.3 (1 H, s, NH), 7.6-6.6 (9 H, m, Arom H), 5.1 (1H, s, Arom H2), 4.1-3.4 (2 H, m, NCH_2), 1.9-0.9 (11 H, m, $4xCH_2+CH_3$). ^{13}C NMR ($CDCl_3$) δ ppm : 161.6 (CO), 142.7 (Arom C), 135.3 (Arom C), 129.7 (2xArom CH), 128.9 (Arom CH), 128.4 (2xArom CH), 127.9 (Arom C), 127.9 (Arom C), 124.2 (Arom CH), 122.0 (Arom CH), 120.0 (Arom CH), 111.5 (Arom CH), 106.8 (Arom CH), 51.0 (NCH_2), 31.5 (CH_2), 27.5 (CH_2), 26.5 (CH_2), 22.5 (CH_2), 13.9 (CH_3). mp 155°C. Anal. Calcd for $C_{21}H_{24}ON_2$: C, 78.71, H, 7.54, N, 8.74. Found : C, 78.23, H, 7.50, N, 8.80.

N-Hexyl-N-phenyl-2-[(5-hydroxy]methylindole] carboxamide **5g, R^1=Me, R^2=Ph, R^3=*n*-C_6H_{13}**

IR (NaCl) 3344 (OH), 2931-2857 (C-H), 1619 (CO). ^1H NMR ($CDCl_3$) δ ppm : 7.30-6.61 (9 H, m, Arom H+OH), 5.75 (1 H, s, Arom H2), 4.00-3.64 (2 H, m, NCH_2), 3.78 (3 H, s, NMe), 1.71-0.75 (11 H, m, $4xCH_2+CH_3$). ^{13}C NMR ($CDCl_3$) δ ppm : 163.7 (CO), 150.1 (Arom COH), 143.0 (Arom C), 133.0 (Arom C), 132.4 (Arom C), 129.1 (Arom CH), 127.2 (Arom CH), 126.9 (Arom CH), 126.4 (Arom C), 114.0 (Arom CH), 110.0 (Arom CH), 106.0 (Arom CH), 105.3 (Arom CH), 50.3 (NCH_2), 31.3 (NMe), 31.3 (CH_2), 27.5 (CH_2), 26.4 (CH_2), 22.4 (CH_2), 13.8 (CH_3). mp 90°C. Anal. Calcd for $C_{22}H_{26}O_2N_2$: C, 75.39, H, 7.47, N, 7.99. Found : C, 75.27, H, 7.39, N, 7.89.

N-Hexyl-N-phenyl-2-[(5-ethylthio)methylndole] carboxamide **6g, R^1=Me, R^2=Ph, R^3=*n*-C_6H_{13}, R^4=Et**

IR (NaCl) 2955-2928-2857 (C-H), 1640 (CO). ^1H NMR ($CDCl_3$) δ ppm : 7.40-6.80 (8 H, m, Arom H), 5.65 (1 H, s, Arom H2), 4.00-3.70 (2 H, m, NCH_2), 3.85 (3 H, s, NMe), 3.00-2.50 (2 H, q, SCH_2), 2.00-0.70 (14 H, m+t, $4xCH_2+CH_3+SCH_2\underline{C}H_3$). ^{13}C NMR ($CDCl_3$) δ ppm : 162.8 (CO), 143.2 (Arom C), 136.7 (Arom CS), 133.0 (Arom C), 129.1 (2xArom CH), 127.3 (3xArom CH), 126.9 (Arom CH), 126.6 (Arom C), 125.7 (Arom C), 125.0 (Arom CH), 110.0 (Arom CH), 106.2 (Arom CH), 50.2 (NCH_2), 31.5 (NMe), 31.4 (CH_2), 29.8 (SCH_2), 27.6 (CH_2), 26.4 (CH_2), 22.4 (CH_2), 14.5 ($SCH_2\underline{C}H_3$), 13.9 (CH_3). Anal. Calcd for $C_{24}H_{30}ON_2S$: C, 73.05, H, 7.66, N, 7.10, S, 8.12. Found : C, 72.88, H, 7.73, N, 7.12, S, 7.82.

N-Hexyl-N-phenyl-2-methylindole carboxamide **7g, R^1=Me, R^2=Ph, R^3=*n*-C_6H_{13}**

IR (NaCl) 3060-2928-2857 (C-H), 1640 (CO). ^1H NMR ($CDCl_3$) δ ppm : 7.4-6.5 (9 H, m, Arom H), 5.7 (1 H, s, Arom H2), 4.2-3.5 (2 H, m, NCH_2), 3.8 (3 H, s, NMe), 1.9-0.7 (11 H, m, $4xCH_2+CH_3$). ^{13}C NMR ($CDCl_3$) δ ppm : 163.1 (CO), 143.3 (Arom C), 137.5 (Arom C), 132.4 (Arom C); 129.1 (2xArom CH), 127.3 (2xArom CH), 126.8 (Arom CH), 126.0 (Arom C), 123.1 (Arom CH), 121.6 (Arom CH), 119.6 (Arom CH), 109.5 (Arom CH), 106.7 (Arom CH), 50.2 (NCH_2), 31.4 (CH_2), 31.3 (NMe), 27.6 (CH_2), 26.4 (CH_2), 22.4 (CH_2), 13.9 (CH_3). mp 47°C. Anal. Calcd for $C_{22}H_{26}ON_2$: C, 79.00, H, 7.83, N, 8.37. Found : C, 78.68, H, 7.82, N, 8.67.

N-Octyl-N-phenyl-2-(5-hydroxyindole) carboxamide **5h, R^1=H, R^2=Ph, R^3=*n*-C_8H_{17}**

IR (NaCl) 3402 (OH), 3275 (NH), 2929-2850 (C-H), 1615 (CO). ^1H NMR ($CDCl_3$) δ ppm : 10.3 (1 H, s, NH), 7.6-6.5 (9 H, m, Arom H+OH), 5.1 (1 H, s, Arom H2), 4.0-3.6 (2 H, m, NCH_2), 1.9-0.6 (15 H, m, $6xCH_2+CH_3$). ^{13}C NMR ($CDCl_3$) δ ppm : 161.5 (CO), 147.7 (Arom COH), 142.6 (Arom C), 130.7 (Arom C), 130.6 (Arom C), 129.7 (2xArom CH), 128.9 (Arom CH), 128.4 (2xArom CH), 128.2 (Arom C), 115.1 (Arom CH), 112.2 (Arom CH), 106.1 (Arom CH), 105.6 (Arom CH), 51.0 (NCH_2), 31.7 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 27.6 (CH_2), 26.9 (CH_2), 22.6 (CH_2), 14.0 (CH_3). mp 160°C. Anal. Calcd for $C_{23}H_{28}O_2N_2$: C, 75.78, H, 7.74, N, 7.68. Found : C, 76.06, H, 7.76, N, 7.70.

N-Octyl-N-phenyl-2-(5-ethylthioindole) carboxamide **6h, R^1=H, R^2=Ph, R^3=*n*-C_8H_{17}**

IR (NaCl) 3277 (NH), 2952-2930-2853 (C-H), 1615 (CO). ^1H NMR ($CDCl_3$) δ ppm : 10.2 (1 H, s, NH),

7.9-6.9 (8 H, m, Arom H), 5.2 (1H, s, Arom H2), 4.2-3.7 (2 H, m, NCH_2), 3.1-2.6 (2 H, q, SCH_2), 2.2-0.7 (18 H, m+t, $6xCH_2+CH_3+ SCH_2\underline{C}H_3$). ^{13}C NMR ($CDCl_3$) δ ppm : 161.5 (CO), 142.6 (Arom C), 134.6 (Arom CS), 130.4 (Arom C), 128.2 (Arom C), 129.7 (Arom CH), 128.8 (3xArom CH), 128.7 (2xArom CH), 125.9 (Arom C), 125.5 (Arom CH), 112.1 (Arom CH), 106.3 (Arom CH), 51.1 (NCH_2), 31.7 (CH_2), 29.9 (SCH_2), 29.3 (CH_2), 29.1 (CH_2), 27.5 (CH_2), 26.9 (CH_2), 22.5 (CH_2), 14.5 ($SCH_2\underline{C}H_3$), 13.9 (CH_3). mp 87°C. Anal. Calcd for $C_{25}H_{32}ON_2S$: C, 73.48, H, 7.89, N, 6.85, S, 7.84. Found : C, 73.23, H, 7.83, N, 6.89, S, 8.09.

N-Octyl-N-phenyl-2-indolecarboxamide **7h, R^1=H, R^2=Ph, R^3=*n*-C_8H_{17}**

IR (NaCl) 3274 (NH), 2927-2852 (C-H), 1616 (CO). ^1H NMR ($CDCl_3$) δ ppm : 10.1 (1 H, s, NH), 7.6-6.5 (9 H, m, Arom H), 5.1 (1 H, s, Arom H2), 4.2-3.7 (2 H, m, NCH_2), 2.1-0.6 (15 H, m, $6xCH_2+CH_3$). ^{13}C NMR ($CDCl_3$) δ ppm : 161.6 (CO), 142.7 (Arom C), 135.4 (Arom C), 129.7 (2xArom CH), 128.9 (Arom CH), 128.4 (2xArom CH), 127.5 (2xArom C), 124.1 (Arom CH), 122.0 (Arom CH), 119.9 (Arom CH), 111.6 (Arom CH), 106.8 (Arom CH), 51.1 (NCH_2), 31.7 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 27.6 (CH_2), 26.9 (CH_2), 22.5 (CH_2), 14.0 (CH_3). mp 124°C. Anal. Calcd for $C_{23}H_{28}ON_2$: C, 79.26, H, 8.09, N, 8.04. Found : C, 79.12, H, 7.92, N, 7.99.

N-Methyl-N-(3-chlorophenyl)-2-[5-(hydroxy)methylindole] carboxamide **5j, R^1=Me, R^2=3-ClC_6H_4, R^3=Me**

IR (NaCl) 3340 (OH), 2930 (C-H), 1619 (CO). ^1H NMR ($CDCl_3$) δ ppm : 7.4-6.6 (7 H, m, Arom H), 5.8 (1 H, s, Arom H2), 5.1 (1 H, s, OH), 3.8 (3 H, s, NMe), 3.4 (3 H, s, NMe). ^{13}C NMR ($CDCl_3$) δ ppm : 163.9 (CO), 150.1 (Arom COH), 145.7 (Arom C), 134.5 (Arom C), 133.3 (Arom C), 131.5 (Arom C), 130.1 (Arom CH), 127.0 (Arom CH), 126.4 (Arom CH), 125.0 (Arom CH), 126.3 (Arom C), 114.4 (Arom CH), 110.3 (Arom CH), 106.7 (Arom CH), 105.4 (Arom CH), 38.2 (NMe), 31.4 (NMe). mp 142°C. Anal. Calcd for $C_{17}H_{15}O_2N_2Cl$: C, 64.86, H, 4.80, N, 8.90, Cl, 11.26. Found : C, 64.90, H, 4.84, N, 8.87, Cl, 11.55.

N-Methyl-N-(3-chlorophenyl)-2-(methylindole) carboxamide **7j, R^1=Me, R^2=3ClC_6H_4, R^3=Me**

IR (NaCl) 3059-2943 (C-H), 1648 (CO). ^1H NMR ($CDCl_3$) δ ppm : 7.50-6.90 (8 H, m, Arom H), 6.07 (1 H, s, Arom H2), 3.92 (3 H, s, NMe), 3.45 (3 H, s, NMe). ^{13}C NMR ($CDCl_3$) δ ppm : 163.3 (CO), 145.9 (Arom C), 137.7 (Arom C), 134.5 (Arom C), 131.3 (Arom C), 130.0 (Arom CH), 126.9 (Arom CH), 126.4 (Arom CH), 125.0 (Arom CH), 125.8 (Arom C), 123.5 (Arom CH), 121.7 (Arom CH), 119.9 (Arom CH), 109.6 (Arom CH), 107.4 (Arom CH), 38.0 (NMe), 31.4 (NMe). Anal. Calcd for $C_{17}H_{15}ON_2Cl$: C, 68.33 H, 5.06, N, 9.37, Cl, 11.86. Found : C, 68.37, H, 5.22, N, 8.98, Cl, 11.90.

Acknowledgment: We thank ADIR for financial support and the referees for their critics and useful suggestions.

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(*Received in Belgium* 25 *May* 1994; *accepted* 28 *September* 1994)