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Synthesis of Some New Fluorine Containing 3-Dialkylaminomethyl Indoles, 3-Indolylglyoxamides and Tryptamines**

Krishna C. Joshi[a, *], **Vijai N. Pathak**[a], and **Raj Pal Singh**[b]

[a] Department of Chemistry, University of Rajasthan, Jaipur-302004, India

[b] Department of Chemistry, J. V. College, Baraut-250611, India

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Several new 2-(fluoroaryl)-3-dialkylaminomethylindoles, 3-acetyl-2-(fluoroaryl)-indoles, 2-(fluoroaryl)-3-indolylglyoxamides and corresponding tryptamines have been prepared as possible psychopharmacological agents. 2-(Fluoroaryl)-indoles have been synthesized by the *Fischer* indole synthesis. 2-(Fluoroaryl)-indoles on treatment with oxalyl chloride and subsequent reaction with amines, gave 2-(fluoroaryl)-3-indolylglyoxamides. Some of these indolylglyoxamides were reducted with lithium aluminium hydride, to the corresponding tryptamines. 2-(Fluoroaryl)-indoles when subjected to *Mannich* reaction afforded 3-dialkylaminomethyl-2-(fluoroaryl)-indoles. All these new compounds have been characterized by IR spectral studies.

(Keywords: Indoles; Mannich reaction; Tryptamines)

Synthese einiger neuer Fluor enthaltender 3-Dialkylaminomethyl-indole, 3-Indolylglyoxamine und Tryptamine

Die Titelverbindungen wurden wegen eventueller psychopharmakologischer Wirksamkeit synthetisiert. 2-(Fluoraryl)-indole wurden nach der *Fischer* schen Indolsynthese hergestellt, 2-(Fluoraryl)-3-indolyl-glyoxamide durch Behandlung mit Oxalylchlorid und Aminen. Reduktion ergab die entsprechenden Tryptamine. Außerdem wurden die 2-(Fluoraryl)-indole mittels *Mannich*-Reaktion in 3-Dialkylaminomethyl-2-(fluoraryl)-indole übergeführt. Die Infrarotspektren aller neuen Verbindungen wurden untersucht.

Introduction

Recently, we have undertaken a comprehensive programme of developing new biologically active organofluorine compounds and have reported the synthesis and CNS activities of a number of fluorine containing 3-indolylglyoxamides, tryptamines, 3-dialkylaminomethyl indoles, 3-dialkylaminoacyl indoles and bisindolyl methanes[1,2].

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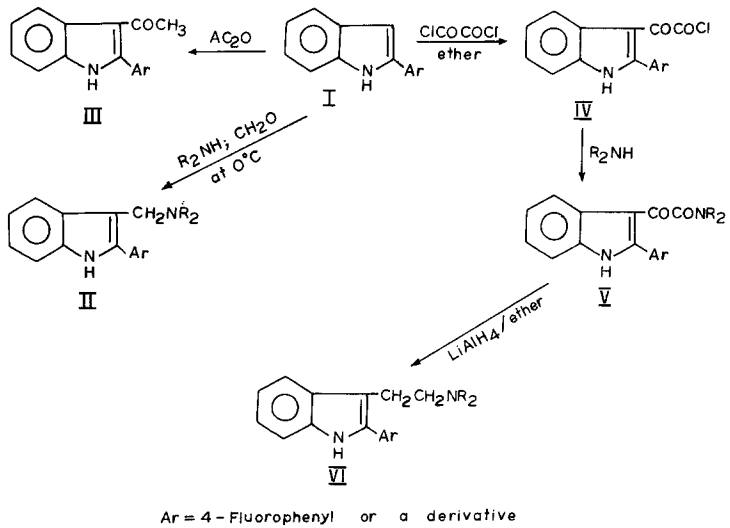
The importance of the indole nucleus is well established in the field of pharmaceutical chemistry and in the plant and animal biochemistry[3–7]. Various psychopharmacological activities such as hallucinogenic, hypnotic, sedative and antidepressant have been found to be associated with the indole heterocycles and allied compounds[8–10]. Activity like monoamine oxidase inhibition has been increased on introduction of phenyl group at the 2-position of indole ring and 3-alkylamino-2-arylindoles have exhibited potent MAO inhibition activity[11]. Some 3-indolylglyoxamides have been shown to posses CNS depressant activity[12].

We now report the synthesis of some new 2-(fluoroaryl)-indoles (I) and corresponding 3-aryl-2-acyl-indoles (III), 3-indolylglyoxamides (V) and tryptamines (VI). 2-(Fluoroaryl)-indoles have been prepared by *Fischer* indole synthesis. Treatment of 2-(fluoroaryl)-indoles with oxalyl chloride in dry ether at 0 °C afforded 3-indolylglyoxalyl chlorides, which in turn with secondary amines gave 3-indolylglyoxamides. Further, reduction of 3-indolylglyoxamides with lithium aluminium hydride furnished corresponding tryptamines. 2-(Fluoroaryl)-indoles also underwent *Mannich* reaction and afforded the 3-alkylamino-methyl-2-(fluoroaryl)-indoles (Scheme 1).

Scheme 1



Experimental

Melting points of all compounds are uncorrected. I.R. spectra were recorded on Perkin-Elmer (model-337) in nujol mull or in KBr pellets.

2-(Fluoroaryl)-indoles

Appropriate phenyl hydrazones of 2-fluorinated acetophenones were cyclized with polyphosphoric acid (P.P.A.) to yield corresponding 2-(fluoroaryl)-indoles. Characteristics and analytical data of the 2-(fluoroaryl)-indoles are given in Table 1.

3-Dialkylaminomethyl-2-(fluoroaryl)-indoles[13]

To a cooled mixture of secondary amine (0.02 mol) and formaldehyde (0.8 ml; 30%) in glacial acetic acid (5.0 ml) was added appropriate 2-(fluoroaryl)-indole (0.01 mol) with constant stirring and allowed to stand overnight at room

Table 1. *2-(Fluorophenyl)-indoles and their 3-acetyl derivatives (I and III in Scheme 1)*

No.	Substituent in *Ar*	*R* at C3	Yield (%)	M.P., °C	Molecular Formula[b]
1[a]	4-F	H	88	190	$C_{14}H_{10}FN$
2	4-F	$COCH_3$	81	226	$C_{16}H_{12}FNO$
	2,4-*DNP* Deriv.		—	257	$C_{22}H_{16}FN_5O_4$
3	4-F, 3-CH_3	H	91	155	$C_{15}H_{12}FN$
4	4-F, 3-CH_3	$COCH_3$	76	231	$C_{17}H_{14}FNO$
	2,4-*DNP* Deriv.		—	264	$C_{23}H_{18}FN_5O_4$
5	4-F, 2-CH_3	H	85	111	$C_{15}H_{12}FN$
6	2-F, 5-CH_3	H	89	116	$C_{15}H_{12}FN$
7[a]	3-Cl, 4-F	H	72	179	$C_{14}H_9ClFN$
8	3-Cl, 4-F	$COCH_3$	71	257	$C_{16}H_{11}ClFNO$
	2,4-*DNP* Deriv.		—	272	$C_{23}H_{17}ClFN_5O_4$
9	2-Cl, 4-F	H	76	96	$C_{14}H_9FN$
10[a]	3-F, 4-OCH_3	H	91	185	$C_{15}H_{12}FNO$

[a] Compounds No. 1, 7 and 10 have been reported in the literature (see Refs.[26–28]).

[b] All new compounds gave satisfactory C, H and N analyses.

temperature. The reaction mixture was then poured into water, and the separated solid was filtered off. The filtrate was made alkaline with sodium hydroxide (10%) solution to afford the desired 3-dialkylaminomethyl-2-(fluoroaryl)-indoles. The crude products were recrystallized with ethanol/methanol. All 3-dialkylaminomethyl-2-(fluoroaryl)-indoles with their characteristics and analytical data are recorded in Table 2.

3-Acetyl-2-(fluoroaryl)-indoles[14]

A mixture of 2-(fluoroaryl)-indole (5.0 g), glacial acetic acid (5.0 ml) and acetic anhydride (150.0 ml) was refluxed for 24 h. Excess acetic anhydride and acetic acid were removed in vacuo, the resultant product was poured into water and filtered. The solid mass was dissolved in ethanol (25.0 ml) and sodium hydroxide solution (2 *N*, 10 ml) by stirring with heating on a water-bath. The resultant solution was diluted with water and filtered off. The residual solid was

recrystallized from ethanol and gave a single spot on TLC. The 3-acetyl-2-(fluoroaryl)-indoles have been characterized by the 2,4-dinitrophenylhydrazones (Table 1).

Table 2. *2-(Fluorophenyl)-3-dialkylaminomethylindoles (II in Scheme 1)*

No.	Substituents in *Ar*	NR_2	Yield (%)	M. P. (°C)	Molecular formula[b]
1	4-F	Diethylamino	91	101	$C_{19}H_{21}FN_2$
2	4-F	Dimethylamino	96	135	$C_{17}H_{17}FN_2$
3	4-F	Morpholino	97	179	$C_{19}H_{19}FN_2O$
4	4-F	Piperidino	97	120	$C_{20}H_{21}FN_2$
5	4-F, 3-CH_3	Diethylamino	88	69 oxalate 192	$C_{20}H_{23}FN_2$
6	4-F, 3-CH_3	Dimethylamino	97	103 oxalate 175.5	$C_{18}H_{19}FN_2$
7	4-F, 3-CH_3	Morpholino	19	180	$C_{20}H_{21}FN_2O$
8	4-F, 3-CH_3	Piperidino	79	119	$C_{21}H_{23}FN_2$
9[a]	4-F, 2-CH_3	Diethylamino	81	202	$C_{22}H_{25}FN_2O_4$
10	4-F, 2-CH_3	Dimethylamino	79	164	$C_{18}H_{19}FN_2$
11	4-F, 2-CH_3	Morpholino	44	140	$C_{20}H_{21}FN_2O$
12	4-F, 2-CH_3	Piperieino	66	105	$C_{21}H_{23}FN_2$
13[a]	2-F, 5-CH_3	Diethylamino	65	75 oxalate 199	$C_{20}H_{23}FN_2$
14	2-F, 5-CH_3	Dimethylamino	71	225	$C_{20}H_{21}FN_2O_4$
15	2-F, 5-CH_3	Morpholino	72	147	$C_{20}H_{21}FN_2O$
16	2-F, 5-CH_3	Piperidino	31	130	$C_{21}H_{23}FN_2$
17	3-Cl, 4-F	Diethylamino	36	92	$C_{19}H_{20}ClFN_2$
18	3-Cl, 4-F	Dimethylamino	77	129	$C_{17}H_{16}ClFN_2$
19	3-Cl, 4-F	Morpholino	45	206-207	$C_{19}H_{18}ClFN_2O$
20	3-Cl, 4-F	Piperidino	41	73	$C_{20}H_{20}ClFN_2$
21	2-Cl, 4-F	Diethylamino	91	87	$C_{19}H_{20}ClFN_2$
22	2-Cl, 4-F	Dimethylamino	94	149	$C_{17}H_{16}ClFN_2$
23	2-Cl, 4-F	Morpholino	59	148	$C_{19}H_{18}ClFN_2O$
24	2-Cl, 4-F	Piperidino	56	88	$C_{20}H_{20}ClFN_2$
25[a]	3-F, 4-OCH_3	Diethylamino	22	194	$C_{22}H_{25}FN_2O_5$
26	3-F, 4-OCH_3	Dimethylamino	28	105	$C_{18}H_{19}FN_2O$
27	3-F, 4-OCH_3	Morpholino	9	174	$C_{20}H_{21}FN_2O_2$
28	3-F, 4-OCH_3	Piperidino	45	139	$C_{21}H_{23}FN_2O$

[a] Compound No. 9, 14 and 25 were isolated as their oxalates. Oxalates of Compound No. 5, 6 and 13 were also prepared.

[b] All compounds gave satisfactory N analyses; in many cases also C, H and/or F analyses were performed.

2-(Fluoroaryl)-3-indolylglyoxalyl chlorides

To a cooled solution of 2-(fluoroaryl)-indole (0.01 mol) in dry ether (20 ml), was added oxalyl chloride (0.012 mol) in dry ether (5.0 ml) with stirring in the course of 15 min. The reaction mixture was further stirred for 10-15 min. and

then diluted with petroleum-ether (60-80°). The residual solid was filtered and used for preparation of 3-indolylglyoxamides without further purification. However, melting points and yields of crude 3-indolylglyoxalyl chlorides were noted: 2-(4-fluorophenyl)-3-indolylglyoxalyl chloride, m.p. 145°, yield 80%; 2-(4-fluoro-3-methylphenyl)-3-indolylglyoxalylchloride, m.p. 148°, yield 73%; 2-(4-fluoro-2-methylphenyl)-3-indolylglyoxalyl chloride, m.p. 109° (dec.), yield 71.5%, 2-(2-fluoro-5-methylphenyl)-3-indolylglyoxalyl chloride, m.p. 154° (dec.), yield 86%; 2-(3-chloro-4-fluorophenyl)-3-indolylglyoxalyl chloride, m.p. 209 °C, yield 90.5%; 2-(2-chloro-4-fluorophenyl)-3-indolylglyoxalyl chloride, m.p. 102°, yield 92.5%.

2-(Fluoroaryl)-3-indolylglyoxamides[1]

The ethereal solution of 2-(fluoroaryl)-3-indolylglyoxalyl chloride (0.01 mol; in 100 ml ether) was added dropwise to an ethereal solution of secondary amine (0.02 mol in 50 ml ether) or diamine (0.015 mol in 50 ml ether) with constant stirring. The solid obtained was filtered, washed with ether and water, and recrystallized from ethanol. All compounds gave single spots in TLC. 2-(fluoroaryl)-3-indolylglyloxamides with their analytical data are given in Table 3.

β-[3-(2-Arylindolyl)]-ethylamines (Tryptamines)[1]

To a suspension of lithium aluminium hydride (2.0 g) in dry ether (100 ml), was added a portion of slurry of 3-indolylglyoxamide (1.5 g in 50 ml ether) and 20 ml benzene. The addition was slowly done to avoid vigorous initial reaction and the reaction mixture was heated under reflux for 6 h on a water bath. After cooling, excess of lithium aluminium hydride was decomposed by the addition of ethyl acetate (10.0 ml) or moist ether (50.0 ml) in the first instance followed by addition of above mixture to the sodium hydroxide solution (2 *N*; 100 ml). This mixture was extracted with ether (3 × 50 ml) and the combined ethereal layers were dried and evaporated to give corresponding tryptamine. All synthesized tryptamines were recrystallized with benzene and were homogeneous on TLC plates. The fluorine containing tryptamines are compiled in the Table 4.

Infrared Spectra

2-(Fluorophenyl)-indoles and their acetyl derivatives exhibit in their IR spectra a strong band between 3,470-3,420 cm^{-1} due to > NH stretching vibrations[20,21]. This is in harmony with the observation of *Hinmann* et al[15]. The strong bands in the range 1,275-1,200 cm^{-1} have been attributed to *Ar*—F stretching modes[16,17]. The C—N frequencies have been assigned to the 1,200-975 cm^{-1} region[25].

In 3-acetylindole derivatives the N—H stretching band is shifted towards lower wavenumbers (3,375-3,125 cm^{-1}) due to the presence of the C=O group at position 3 of the indole ring[18,19]. C=O absorption occures between 1,620-1,605 cm^{-1} [18,22,23]. Conjugation of C=O with the indole ring is responsible for the lowering of the C=O absorption (1,725-1,620 cm^{-1}). One of the special features of the acetylated indoles is the occurrence of two broad strong peaks in the N—H stretching region. This may be due to the intermolecular hydrogen bonding between the N—H group of one molecule and the C=O group of the second molecule. If C=O is removed by the formation of 2,4-dinitrophenylhydrazone derivative, there remains only one band in this region.

Table 3. *2-(Fluoroaryl)-3-indolylglyoxamides (V in Scheme 1)*

No.	Substituents in *Ar*	—NR_2 or —NN—	Yield (%)	M.P. (°C)	Molecular Formula[a]
1	4-F	Diethylamino	44	142	$C_{20}H_{19}FN_2O_2$
2	4-F	Dimethylamino	93	231	$C_{18}H_{15}FN_2O_2$
3	4-F	Morpholino	79	129 (dec)	$C_{20}H_{17}FN_2O_3$
4	4-F	Piperidino	91	224–225	$C_{21}H_{19}FN_2O_2$
5	4-F, 3-CH_3	Diethylamino	37	140	$C_{21}H_{21}FN_2O_2$
6	4-F, 3-CH_3	Dimethylamino	87	226	$C_{19}H_{17}FN_2O_2$
7	4-F, 3-CH_3	Morpholino	87	191	$C_{21}H_{19}FN_2O_3$
8	4-F, 3-CH_3	Piperidino	80	220	$C_{22}H_{21}FN_2O_2$
9	4-F, 2-CH_3	Diethylamino	88	193	$C_{21}H_{21}FN_2O_2$
10	4-F, 2-CH_3	Dimethylamino	96	250	$C_{19}H_{17}FN_2O_2$
11	4-F, 2-CH_3	Morpholino	68	135 (dec)	$C_{21}H_{19}FN_2O_3$
12	4-F, 2-CH_3	Piperidino	67	215	$C_{22}H_{21}FN_2O_2$
13	2-F, 5-CH_3	Diethylamino	85	159	$C_{21}H_{21}FN_2O_2$
14	2-F, 5-CH_3	Dimethylamino	93	177	$C_{19}H_{17}FN_2O_2$
15	2-F, 5-CH_3	Morpholino	82	177	$C_{21}H_{19}FN_2O_3$
16	2-F, 5-CH_3	Piperidino	83	206	$C_{22}H_{21}FN_2O_2$
17	3-Cl, 4-F	Diethylamino	54	160	$C_{20}H_{18}ClFN_2O_2$
18	3-Cl, 4-F	Dimethylamino	90	246	$C_{18}H_{14}ClFN_2O_2$
19	3-Cl, 4-F	Morpholino	78	212	$C_{20}H_{16}ClFN_2O_3$
20	3-Cl, 4-F	Piperidino	83	180	$C_{21}H_{18}ClFN_2O_2$
21	2-Cl, 4-F	Diethylamino	75	152	$C_{20}H_{18}ClFN_2O_2$
22	2-Cl, 4-F	Dimethylamino	90	232	$C_{18}H_{14}ClFN_2O_2$
23	2-Cl, 4-F	Morpholino	78	141	$C_{20}H_{16}ClFN_2O_2$
24	2-Cl, 4-F	Piperidino	83	217	$C_{21}H_{18}ClFN_2O_2$
25	4-F	Piperazino	97	> 350	$C_{36}H_{26}F_2N_4O_4$
26	4-F, 3-CH_3	Piperazino	90	> 350	$C_{38}H_{30}F_2N_4O_4$
27	4-F, 2-CH_3	Piperazino	93	> 350	$C_{38}H_{30}F_2N_4O_4$
28	2-F, 5-CH_3	Piperazino	96	242 (dec)	$C_{38}H_{30}F_2N_4O_4$
29	3-Cl, 4-F	Piperazino	82	332 (dec)	$C_{36}H_{24}Cl_2F_2N_4O_4$
30	2-Cl, 4-F	Piperazino	88	310 (dec)	$C_{36}H_{24}Cl_2F_2N_4O_4$

[a] See footnote[b] Table 2.

In the IR spectra of 2-(fluorophenyl)-3-dialkylaminomethylindoles, the N—H stretching vibration band appears between 3,420 and 3,250 cm^{-1} [24,25]. For the compounds No. **5, 6, 9, 13** and **25** (Table 2), which have been isolated as oxalates, $\overset{+}{N}H$ stretching absorption occurs between 2,675–2,475 cm^{-1} [28,29]. These salts show also C=O bands above 1,710 cm^{-1}. Further, in the oxalates a strong band appears at 690 cm^{-1} which has been attributed to $^-OOC—COO^-$ wagging absorption[23].

3-Indolylglyoxamides show N—H bands between 3,250 and 3,140 cm^{-1}. The shifting of the band to lower region is due to the presence of electronegative COCO groups at position 3 of the indole ring[19]. The C=O-bands occur in the region of 1,670-1,500 cm^{-1} [18,20,21]; the one at higher wave number may be attributed to the amide C=O and another at lower wave number to the keto group. In the reduction products (Table 4), the strong bands between

1,670–1,500 cm^{-1} disappear and N—H absorption occurs between 3,440 and 3,200 cm^{-1}. The *Ar*—F stretching vibrations cause absorption between 1,285 and 1,200 cm^{-1} [16, 17].

Table 4. *Tryptamines (VI in Scheme 1)*

No.	Substituents in *Ar*	NR_2	Yield (%)	M.P. (°C)	Molecular formula[a]
1	4-F	Dimethylamino	43	94–96	$C_{18}H_{19}FN_2$
2	4-F	Morpholino	83	142	$C_{20}H_{21}FN_2O$
3	4-F	Piperidino	83	176	$C_{21}H_{23}FN_2$
4	4-F, 3-CH_3	Dimethylamino	82	148	$C_{19}H_{21}FN_2$
5	4-F, 3-CH_3	Morpholino	65	173	$C_{21}H_{23}FN_2O$
6	4-F, 2-CH_3	Dimethylamino	77	152–153	$C_{19}H_{21}FN_2$
7	4-F, 2-CH_3	Piperidino	51	168–170	$C_{22}H_{25}FN_2$
8	2-F, 5-CH_3	Dimethylamino	80	86	$C_{19}H_{21}FN_2$
9	2-F, 5-CH_3	Morpholino	36	143	$C_{21}H_{23}FN_2O$
10	2-F, 5-CH_3	Piperidino	50	127–128	$C_{22}H_{25}FN_2$
11	3-Cl, 4-F	Morpholino	74	134–136	$C_{20}H_{22}ClFN_2O$

[a] In all cases satisfactory N, C and H analyses were obtained.

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