SYNTHESIS AND STRUCTURE OF NEW OXOINDOLES

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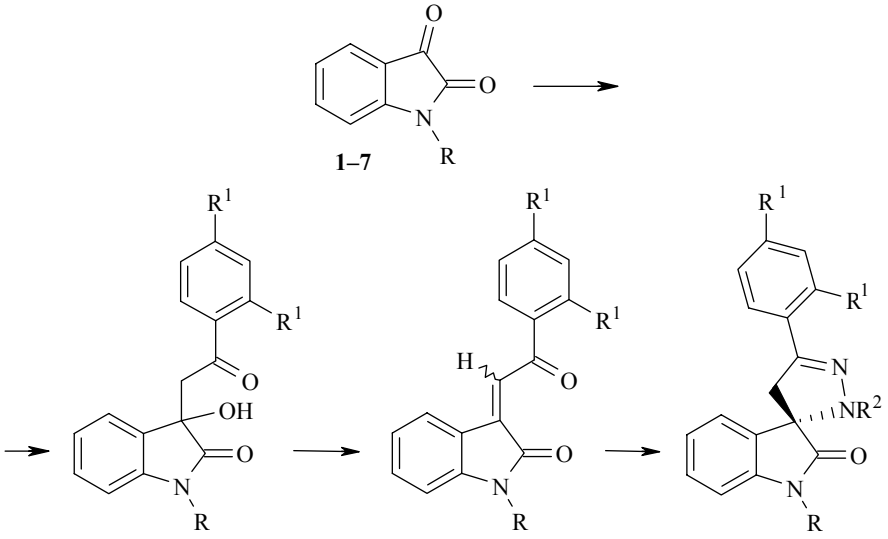
The synthesis and study of the structure of new oxoindoles has been carried out. The molecular and crystal structure, and the stereochemistry atom of C(3) of 1,2-diacetyl-5'-phenyl(2',4'dihydrospiro[3H-indol-3,3'-[3H]pyrazol]-2-(1H)-one have been established by X-ray crystallography.

Keywords: oxoindole, 3-(2-aryl-2-oxoethylidene)-2-indolinones, spirooxoindoles, X-ray crystallography.

Derivatives of indole, which are widely distributed in nature, are of primary importance for living creatures, and such compounds, not extracted from natural sources, are used as medicinals. As in the past this is a stimulus for the development of new methods of synthesis for both known and new derivatives of indole [1-5]. 3-(2-Aryl-2-oxoethylidene)-2-indolinones and products of their heterocyclization, which have a variety of physiological activities are of especial interest [6-14].



1–7 **8–17** **18–27** **28–33**

1,8,11,18,19,28,29 R = H, **2,9,12,20,21,30** R = Me, **3,10,13,22,23,31,33** R = Et, **4,14,24** R = *n*-Bu, **5,15,25** R = *n*-C_6H_{13}, **6,16,26** R = *n*-C_9H_{19}, **7,17,27** R = *n*-$C_{10}H_{21}$, **32** R = Ac; **8–10,18,20,22,28,32** R^1 = H, **11–17, 19,21, 23–27, 29–31, 33** R^1 = Cl; **28–31** R^2 = H, **32,33** R^2 = Ac

* Deceased.

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With the objectives of broadening the range of compounds in the oxoindole series with potential biological activity and in continuing our study of synthetic reactions of indoline-2,3-dione (**1**) [15-18] we have investigated suitable routes for its conversion into 1-alkylindoline-2,3-diones **2-7** and compounds **8-13**.

Table 1. Properties and Characteristics of the Synthesized Compounds **8-33**

Compound	Empirical formula	Found, % / Calculated, %				mp, °C*	Yield, %
		C	H	Cl	N		
8	$C_{16}H_{13}NO_3$	71.90 / 71.68	4.90 / 4.73	—	5.24 / 5.21	178-180	79
9	$C_{17}H_{15}NO_3$	72.58 / 72.49	5.37 / 5.06	—	4.98 / 4.90	172-175	75
10	$C_{18}H_{17}NO_3$	73.20 / 73.24	5.80 / 5.70	—	4.74 / 4.60	120-121	68
11	$C_{16}H_{11}Cl_2NO_3$	57.17 / 57.20	3.30 / 3.09	21.09 / 21.28	4.17 / 4.07	164-165	41
12	$C_{17}H_{13}Cl_2NO_3$	58.31 / 58.18	3.74 / 3.72	20.25 / 20.09	4.00 / 4.12	161-164	90
13	$C_{18}H_{15}Cl_2NO_3$	59.36 / 59.30	4.15 / 3.91	19.47 / 19.39	3.85 / 4.00	135-138	62
14	$C_{20}H_{19}Cl_2NO_3$	61.24 / 60.77	4.88 / 4.74	18.08 / 18.13	3.57 / 3.71	Oil	95
15	$C_{22}H_{23}Cl_2NO_3$	62.86 / 62.41	5.52 / 5.82	16.87 / 16.88	3.33 / 3.30	Oil	91
16	$C_{25}H_{29}Cl_2NO_3$	64.94 / 64.82	6.32 / 6.21	15.33 / 15.28	3.03 / 2.96	Oil	94
17	$C_{26}H_{31}Cl_2NO_3$	65.54 / 64.97	6.56 / 6.61	14.88 / 14.83	2.94 / 3.13	Oil	97
18	$C_{16}H_{11}NO_2$	77.10 / 76.99	4.45 / 4.77	—	5.62 / 5.38	195-197	88
19	$C_{16}H_9Cl_2NO_2$	60.40 / 60.33	2.85 / 2.90	22.29 / 22.17	4.40 / 4.32	226-227	59
20	$C_{17}H_{13}NO_2$	77.55 / 77.53	4.98 / 4.87	—	5.32 / 5.19	131-132	85
21	$C_{17}H_{11}Cl_2NO_2$	61.47 / 60.99	3.34 / 3.59	21.35 / 21.17	4.22 / 4.45	175-176	94
22	$C_{18}H_{15}NO_2$	77.96 / 77.93	5.45 / 5.44	—	5.05 / 4.91	131-132	79
23	$C_{18}H_{13}Cl_2NO_2$	62.45 / 62.51	3.78 / 3.78	20.48 / 20.52	4.05 / 4.39	98-100	98
24	$C_{20}H_{17}Cl_2NO_2$	64.18 / 64.02	4.58 / 4.41	18.95 / 18.99	3.74 / 3.90	Oil	94
25	$C_{22}H_{21}Cl_2NO_2$	65.68 / 65.81	5.26 / 5.10	17.62 / 17.59	3.48 / 3.37	Oil	97
26	$C_{25}H_{27}Cl_2NO_2$	67.57 / 67.89	6.12 / 6.14	15.96 / 15.83	3.15 / 3.30	Oil	93
27	$C_{26}H_{29}Cl_2NO_2$	68.12 / 68.00	6.38 / 6.47	15.47 / 15.39	3.06 / 2.87	Oil	96
28	$C_{16}H_{13}N_3O$	72.99 / 72.78	4.98 / 4.76	—	15.96 / 16.07	202-208	66
29	$C_{16}H_{11}Cl_2N_3O$	57.85 / 58.01	3.34 / 3.66	21.35 / 21.22	12.65 / 12.37	224-225	38
30	$C_{17}H_{13}Cl_2N_3O$	58.98 / 58.75	3.78 / 3.77	20.48 / 20.59	12.14 / 12.25	200-201	34
31	$C_{18}H_{15}Cl_2N_3O$	60.01 / 60.00	4.20 / 4.34	19.68 / 19.71	11.66 / 11.78	161-164	35
32	$C_{20}H_{17}N_3O_3$	69.15 / 69.01	4.93 / 4.90	—	12.10 / 11.97	173-174	80
33	$C_{20}H_{17}Cl_2N_3O_2$	59.71 / 59.73	4.26 / 4.39	17.63 / 17.54	10.45 / 10.26	204-207	69

* Solvent for recrystallization: EtOH (compounds **8,10,13,21-23, 30**), *i*-PrOH (compounds **9, 11, 12, 18, 19, 28, 29, 32, 33**), benzene (compounds **20, 31**).

We have previously reported [9] that 3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (**8**) was obtained from the condensation of isatin with acetophenone in dry EtOH. We have established that this conversion can also be carried out in a mixture of H_2O-*i*-PrOH-Et_2NH, which simplified the process without decreasing the yield. Use of these reaction conditions permitted the synthesis of products **9** and **10** (Table 1).

It is known that the presence of halogen atoms in a molecule leads to an increase in or the appearance of biological activity [9, 19, 20]. The oxoindoles **11**-**17** containing the 2,4-dichlorophenyl unit were synthesized from N-alkylisatins **4**-**7** and 2,4-dichloroacetophenone. Note somewhat increased yields of the aldols **11**-**13** in comparison with their analogs **8**-**10** (Table 2).

The standard procedure for dehydration of the alcohols **8**-**17** with a mixture of hydrochloric and ethanolic acids led to a new α,β-unsaturated ketones **18**-**27**, among analogs of which are substances known to be active against *Plasmodium falciparum* [13].

Interaction of enone **18** with hydrazine hydrate gave the spiran **28** in the ^{1}H NMR spectrum of which there are signals for methylene and aromatic protons, and also two NH protons of the pyrazolin (7.92 ppm) and indolinone (10.4) rings respectively. It should be noted that the opposite assignment of these protons was given in [9]. Comparative analysis of the ^{1}H NMR spectra of compounds **28**-**31** confirms our interpretation because substitution of the amide proton by an alkyl substituent led to the extinction in the spectra of compounds **28** and **29** of the signals at 10.40 and 10.53 ppm and the retention of the signals at 8.16 and 7.98 ppm respectively.

Table 2. IR Spectra of Compounds **8**-**33**

Compound	ν, cm^{-1}
8	1670, 1690 (C=O), 3240 (NH), 3270-3350 (OH)
9	1650, 1685 (C=O), 3330-3400 (OH)
10	1655, 1690 (C=O), 3320-3390 (OH)
11	780 (C–Cl), 1645, 1680 (C=O), 3100 (NH), 3290-3350 (OH)
12	775 (C–Cl), 1645, 1680 (C=O), 3330-3390 (OH)
13	775 (C–Cl), 1655, 1690 (C=O), 3200-3400 (OH)
14	775 (C–Cl), 1645, 1680 (C=O), 3230-3400 (OH)
15	780 (C–Cl), 1655, 1675 (C=O), 3300-3400 (OH)
16	770 (C–Cl), 1650, 1685 (C=O), 3240-3400 (OH)
17	780 (C–Cl), 1660, 1685 (C=O), 3380 (OH)
18	1670, 1675 (C=O), 3440 (NH)
19	770 (C–Cl), 1670, 1675 (C=O), 3150 (NH)
20	1665, 1675 (C=O), 3280 (NH)
23	780 (C–Cl), 1670, 1685 (C=O),
24	770 (C–Cl), 1655, 1675 (C=O)
25	785 (C–Cl), 1665, 1670 (C=O)
26	770 (C–Cl), 1655, 1685 (C=O)
27	780 (C–Cl), 1660, 1685 (C=O)
28	1630 (C=N), 3300–3150 (NH)
29	1635 (C=N), 3350–3150 (NH)
30	1630 (C=N), 3300–3150 (NH)
31	780 (C–Cl), 1620 (C=N), 1685 (C=O), 3280 (NH)
32	1635 (C=N), 1655, 1680 (C=O)
33	780 (C–Cl), 1625 (C=N), 1675 (C=O)

* ^{13}C NMR Spectrum, δ, ppm: 175.26, 172.13, 170.42, 167.36, 153.35, 139.0, 130.20, 129.13, 67,45, 26.15, 21.33.

There has been no study of the stereochemistry of the atom C(3) of the spiro compound **28** by X-ray crystallography [21]. We attempted to prepare monocrystals of compound **28** suitable for X-ray crystallography but were unsuccessful. In this connection compound **28** was converted into the acetyl derivative **32**. An investigation of a monocrystal of composition $C_{20}H_{17}N_3O_3$ by X-ray crystallography showed that its molecular

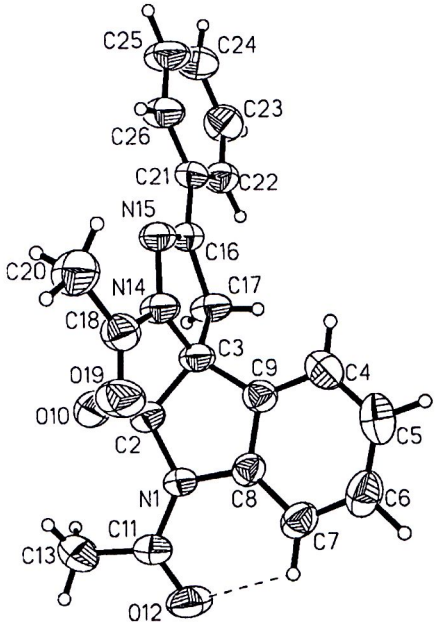

Fig. 1 Molecular structure of compound **32**

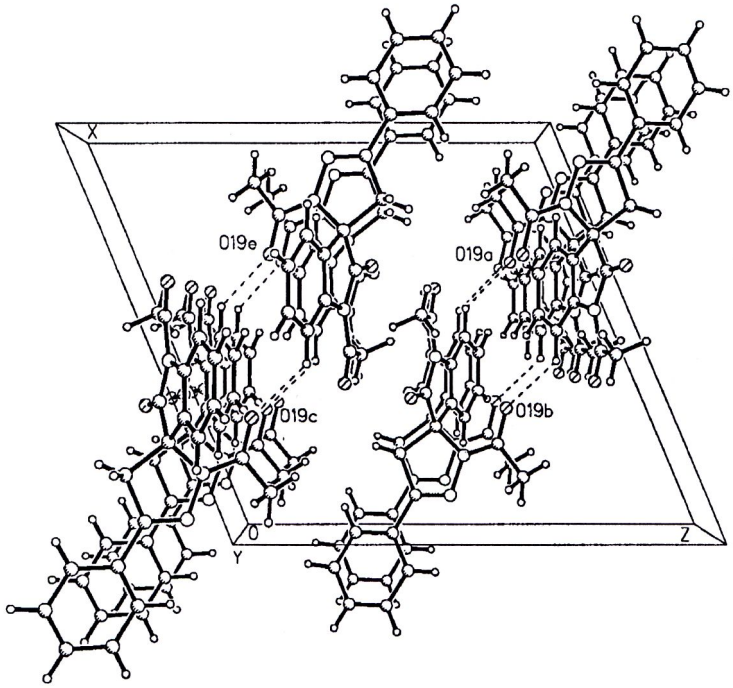

Fig. 2. Crystal structure of compound **32** along the direction [010]

structure consisted of four rings: two phenyl, pyrrolidinyl, and pyrazolinyl (Fig. 1). The aromatic rings lie practically in one plane with adjoining pyrazolin and pyrrollidinone units at dihedral angles of 1.9(1) and 1.6(1)° respectively.

Table 3. ^{1}H NMR Spectra of Compounds **8**-**33**

Com-pound	^{1}H NMR spectrum, δ, ppm. (*J*, Hz)
8	3.58 (1H, s, OH), 3.84, 3.95 (2H, d, d, *J* = 10.8, *J* = 15.2, CH_2), 6.15-7.94 (9H, m, arom.), 10.31 (1H, NH)
9	3.18 (3H, s, CH_3), 3.51, 3.62 (2H, d, d, *J* = 8, *J* = 14.8, CH_2), 4.31 (1H, s, OH), 6.10-7.74 (9H, m, arom.)
10	1.30 (3H, t, *J* = 7.2, CH_3), 3.46-4.01 (4H, m, $2CH_2$), 4.78 (1H, s, OH), 6.61-7.92 (9H, m, arom.)
11	3.58, 3.68 (2H, d, d, *J* = 11.2, *J* = 14.5, CH_2), 6.19 (1H, s, OH), 6.76-7.62 (7H, m, arom.), 10.32 (1H, NH)
12	3.18 (3H, s, CH_3), 3.51, 3.62 (2H, d, d, *J* = 11.5, *J* = 18.3, CH_2), 4.31 (1H, s, OH), 6.10-7.74 (9H, m, arom.)
13	1.27 (3H, t, *J* = 7.2, CH_3), 3.44-3.94 (4H, m, $2CH_2$), 4.65 (1H, s, OH), 6.78-7.52 (7H, m, arom.)
14	0.97-1.34 (7H, m, $CH_3(CH_2)_2$), 3.26-4.01 (4H, m, $CH_3C\underline{H}_2$, NCH_2), 4.63 (1H, s, OH), 6.71-7.73 (7H, m, arom.)
15	0.87-1.47 (11H, m, $CH_3(CH_2)_4$), 3.20-3.89 (4H, m, $CH_3C\underline{H}_2$, NCH_2), 4.57 (1H, s, OH), 6.61-7.79 (7H, m, arom.)
16	0.80-1.25 (15H, m, $CH_3(CH_2)_7$), 3.23-3.92 (4H, m, $CH_3C\underline{H}_2$, NCH_2), 4.70 (1H, s, OH), 6.80-7.71 (7H, m, arom.)
17	0.92-1.46 (17H, m, $CH_3(CH_2)_8$), 3.01-3.93 (4H, m, $CH_3C\underline{H}_2$, NCH_2), 4.57 (1H, s, OH), 6.78-7.67 (7H, m, arom.)
18	6.83-8.14 (9H, m, arom.), 7.71 (1H, s, C=CH), 10.83 (1H, NH)
19	6.84-8.35 (7H, m, arom.), 7.75 (1H, s, C=CH), 10.86 (1H, NH)
20	3.15 (3H, s, CH_3), 6.64-8.27 (9H, m, arom.), 7.78 (1H, c, C=CH)
23	1.20 (3H, t, *J* = 7.2, CH_3), 3.70 (2H, q, *J* = 7.2, CH_2), 6.69-8.52 (7H, m, arom.), 7.51 (1H, s, C=CH)
24	0.90-1.31 (7H, m, $CH_3(CH_2)_2$), 3.06-3.96 (4H, m, $CH_3C\underline{H}_2$, NCH_2), 6.71-7.73 (7H, m, arom.), 7.76 (1H, c, C=CH)
25	0.71-1.32 (11H, m, $CH_3(CH_2)_4$), 3.40-3.59 (4H, m, $CH_3C\underline{H}_2$, NCH_2), 6.60-7.84 (8H, m, arom., C=CH)
26	0.67-1.33 (15H, m, $CH_3(CH_2)_7$), 3.87-3.90 (4H, m, $CH_3C\underline{H}_2$, NCH_2), 6.80-7.77 (8H, m, arom., C=CH)
27	0.82-1.26 (17H, m, $CH_3(CH_2)_8$), 2.85-3.91 (4H, m, $CH_3C\underline{H}_2$, NCH_2), 6.78-7.67 (8H, m, arom., C=CH)
28	3.15-3.95 (2H, m, CH_2), 6.82-7.84 (9H, m, arom.), 7.92 (1H, s, NNH), 10.40 (1H, CONH)
29	3.18-3.65 (2H, m, CH_2), 6.85-7.76 (7H, m, arom.), 8.21 (1H, s, NNH), 10.53 (1H, CONH)
30	3.14 (3H, s, CH_3), 3.37-3.61 (2H, m, CH_2), 6.97-7.78 (7H, m, arom.), 8.16 (1H, s, NNH)
31	1.25 (3H, t, *J*=7.2, CH_3), 3.40-4.01 (4H, m, $2CH_2$), 6.95-7.84 (7H, m, arom.), 7.98 (1H, s, NNH)
32*	2.26, 2.59 (6H, s, s, $2CH_3$), 3.68, 3.75 (2H, d, d, *J* = 8, *J* = 13.3, CH_2), 7.12-8.21 (7H, m, arom.)
33	1.25 (3H, t, *J* = 7.2, CH_3), 2.26 (3H, s, $COCH_3$), 3.46-4.01 (4H, m, $2CH_2$), 6.95-7.84 (7H, m, arom.)

* ^{13}C NMR Spectrum, δ, ppm: 175.26, 172.13, 170.42, 167.36, 153.35, 139.0, 130.20, 129.13, 67,45, 26.15, 21.33.

The dihedral angle formed by the pyrrolidinone and pyrazoline cycles, which form the spiro bond at C(3), is 89.2(1)°. The five membered rings with the benzoyl groups have different compositions, namely: the vicinal coupling at atom C(8)-C(9) with carbon-carbon bond C(16)-C(21) leads to differences in coplanarity of these rings. The displacements of atoms from the least mean squares plane of the pyrazoline ring are: C(3) 0.005, C(2) -0.005, N(1) 0.003, C(8) 0, C(9) -0.003 Å. The displacements of atoms from the pyrrolidinone ring are: C(3) 0.031, N(14) -0.023, C(16) 0.021, C(17) -0.031Å. Evidently in both cases there is a tendency to a *distorted envelope* conformation. The carbonyl atom O(10) is coplanar with the plane of pyrrolidinone ring with a precision of 0.017 Å, while atoms O(12) and C(13) deviate from the latter by -0.206 and 0.256 Å, while the torsion angle O(10)-C(2)-C(3)-C(9) is 0.8°. The acetyl groups do not lie in the planes of the rings, the torsion angles C(8)-N(1)-C(11)-O(12) and C(3)-N(14)-C(18)-O(19) equal -10.9 and 4.6° respectively. The displacements of atoms O(19) and C(20) from the pyrrolidinone unit are -0.377 and -0.421 Å respectively. Thus, taking into account the conformation of the molecule as a whole and the fact that the displacement of atoms N(14) and C(17) of the pyrazoline ring from the least squares plane of the pyrollidinone ring are -1.662(2) and 1.164(3) Å respectively, it may be concluded that C(3) has the *S*-conformation in the investigated structure of **32**. The interatomic distances and bond angles in the pyrazoline and pyrrolidinone rings are not equivalent, In the former N(15)-C(16) has bond order 2, whereas in the second N(1)-C(2) has bond order 1.5, with lengths of 1.286(2) and 1.407(2) Å respectively, which leads to partial delocalization of the electrons in these rings and the neighboring units with formation C=O carbonyl double bonds. Thus the carbonyl atom O(10) of the pyrrolidinone ring and the carbonyl atoms of the acetyl groups O(12) and O(13) have exclusively accept or properties, as a result of which the structure is stabilized by the formation of intramolecular hydrogen bonds C(7)-H(7)…O(12) with the parameters C(7)-H(7) 0.991, C(7)…O(12) 2.848, H(7)…O(12) 2.239 Å, and the angles at the hydrogen atom of 111.7°. This hydrogen bond permits the discussion of an additional six-membered C(7).C(8).N(1)C(11).O(12).H(7) "pseudoring". It is also established that the basic role in the formation of the crystal structure is played by the intermolecular bonds C(7)-H(7)…O(19) [1-*x*, 0.5+*y*, 0.5-*z*] with parameters C(7)-O(19) 3.182(2), H(7)…O(19) 2.50(2) Å and the angle at the hydrogen atom of 126(1)°, which joins crystallographically independent molecules with a symmetrical bond with the production of a centrosymmetric dimer. A portion of the crystal structure along the [010] direction is shown in Fig. 2. Compound **33** was synthesized in conditions analogous to those used for compound **32**.

Thus syntheses of new N-alkylisatins and their aldol condensations with acetophenone and 2,4-dichloroacetophenone have been accomplished, It is shown that the synthesized 3-(2-oxo-2-arylethylidene)-2-indolinones cyclize on reaction with hydrazine hydrate into spiro compounds with *S*-configuration at the C(3) connection.

EXPERIMENTAL

^{1}H and ^{13}C NMR Spectra were recorded on a Bruker AC-80 (80 and 20 MHz) spectrometer in 2-3% $(CD_3)_2SO$ solution for compounds **8**, **11**, **18-20**, **28-30**, $CDCl_3$ for compounds **9**, **10**, **12-17**, **21-27** and CD_3CN for compounds **31**, **33** with TMS as internal standard. IR spectra of nujol mulls were recorded on a Specord 74-1 instrument. Experimental collection of X-ray crystallographic data was carried out on a KM4CCD diffractometer using ω-scanning. Melting points were determine with a Boetius block. The course of reactions and purity of compounds were monitored by TLC on Sorbfil UV-254 strips.

1-Alkylindoline-2,3-diones 2-7. Compounds **2** and **3** were obtained by a known method [18].
Compounds 4-7 were synthesized analogously**.**

1-Butylindoline-2,3-dione (4). A reddish oil, R_f 0.65 ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1735 (C=O). Found, %: C 70.81, H 6.40, N 6.78. Calculated for $C_{12}H_{13}NO_2$, %: C 70.92, H 6.45, N 6.89.

1-Hexylindoline-2,3-dione (5). Reddish oil, R_f 0.60 ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1750 (C=O). Found, %: C 72.51, H 7.44, N 5.97. Calculated for $C_{14}H_{17}NO_2$, %: C 72.70, H 7.41, N 6.06.

1-Nonylindoline-2,3-dione (6). Reddish oil, R_f 0.63 ($CHCl_3$) IR spectrum, ν cm^{-1}: 1745 (C=O). Found, %: C 74.57, H 8.47, N 5.02. Calculated for $C_{17}H_{23}NO_2$, %: 74.69, H 8.48, N 5.12.

1-Decylindoline-2,3-dione (7). Reddish oil, R_f 0.66 ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1735 (C=O). Found, %: C 75.20, H 8.67, N 5.02. Calculated for $C_{18}H_{25}NO_2$, %: C75.22, 8.77, 4.87.

Synthesis of Alcohols 8-17 (General Method). Acetophenone (0.04 mol) (or 2,4-dichloroacetophenone) and diethylamine (2.92 g, 0.04 mol) were added consecutively with stirring to isatin **1** (0.04 mol) or an N-alkylisatin **2-7** in a mixture of water (45 ml) and *i*-PrOH (30 ml) (or EtOH or MeCN). The mixture was stirred for 8 h at room temperature and the precipitate was filtered off, and washed (3×25 ml) with *i*-PrOH (or EtOH or MeCN). The crystalline product was used for further synthesis without purification. For analytical purposes, a sample was recrystallized from a suitable solvent to give:

3-Hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (8), 3-Hydroxy-1-methyl-3-(2-oxo-2-phenyl)indolin-2-one (9), 1-Ethyl-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (10), 3-[2-(2,4-Dichlorophenyl)-2-oxoethyl]-3-hydroxyindolin-2-one (11), 3-[2-(2,4-Dichlorophenyl)-2-oxoethyl]-3-hydroxy-1-methylindolin-2-one (12), 3-[2-(2,4-Dichlorophenyl)-2-oxoethyl]-1-ethyl-3-hydroxyindolin-2-one (13), 1-Butyl-3-[2-(2,4-dichlorophenyl)-2-oxoethyl]-3-hydroxyindolin-2-one (14), 3-[2-(2,4-Dichlorophenyl)-2-oxoethyl]-1-hexyl-3-hydroxyindolin-2-one (15), 3-[2-(2,4-Dichlorophenyl)-2-oxoethyl]-3-hydroxy-1-nonylindolin-2-one (16), and 1-Decyl-3-[2-(2,4-dichlorophenyl)-2-oxoethyl]-3-hydroxyindolin-2-one (17) (Table 1)**.**

Preparation of Enones 18-25 (General Method). Dehydration of the corresponding keto alcohols was carried out by a method analogous to [9] to obtain:

3-(2-Oxo-2-phenylethylidene)-2-indolin-2-one (18), **3-[2-(2,4-Dichlorophenyl)-2-oxoethylidene]-indolin-2-one (19), 1-Methyl-3-(2-oxo-2-phenylethylidene)indolin-2-one (20), 3-[2-(2,4-Dichlorophenyl)-2-oxoethylidene]-1-methylindolin-2-one (21), 1-Ethyl-3-(2-oxo-2-phenylethylidene)indolin-2-one (22), 3-[2-(2,4-Dichlorophenyl)-2-oxoethylidene]-1-ethylindolin-2-one (23), 1-Butyl-3-[2-(2,4-dichlorophenyl)-2-oxoethylidene]indolin-2-one (24), 3-[2-(2,4-Dichlorophenyl)-2-oxoethylidene]-1-hexylindolin-2-one (25), 3-[2-(2,4-Dichlorophenyl)-2-oxoethylidene]-1-nonylindolin-2-one (26), and 1-Decyl-3-[2-(2,4-dichlorophenyl)-2-oxoethylidene]indolin-2-one (27),** (Table 1).

Preparation of Pyrazolinyloxoindoles 28-31 (General Method). A mixture of the initial enone (0.005 mol) and 98% hydrazine hydrate (0.006 mol) in absolute ethanol (35 ml) was refluxed for 4-8 h until the reaction was completed (monitored by TLC). The mixture was left overnight, the residue was separated, and recrystallized from a suitable solvent to give:

5'-Phenyl-2',4'-dihydrospiro[3H-indole-3,3'-[3H]-pyrazol]-2(1H)-one (28), 5'-(2,4-Dichlorophenyl)-2',4'-dihydrospiro[3H-indole-3,3'-[3H]-pyrazol]-2(1H)-one (29), 5'-(2,4-Dichlorophenyl)-2',4'-dihydrospiro-[3H-indole-3,3'-[3H]-pyrazol]-1-methyl-2(1H)-one (30), 5'-(2,4-Dichlorophenyl)-2',4'-dihydrospiro[3H-indol-3,3'-[3H]-pyrazol]-1-ethyl-2(1H)-one (31) (Table 1).

Acetylation of pyrazolinoxoindoles (General Method). Pyridine (0.079g, 0.001 mol) was added to a suspension of a pyrazolindole (0.005 mol) in Ac_2O (7.65 g, 0.0075 mol) and the mixture was heated at 95-100°C for 5 h. The mixture was cooled to room temperature, water (2 ml) was added, and after stirring for 2.5 h, the precipitate was filtered off, washed with water (15 ml) and then *i*-PrOH (2 ml). The residue was dried over NaOH in vacuum and then recrystallized from a suitable solvent to give:

1,2'-Diacetyl-5'-phenyl-2',4'-dihydrospiro[3H-indole-3,3'-[3H]-pyrazol]-2(1H)-one (32) and 2'-Acetyl-5'-(2,4-dichlorophenyl)-1-ethyl-2',4'-dihydrospiro[3H-indole-3,3'-[3H]-pyrazol]-2(1H)-one (33) (Table 1).

X-ray crystallographic analysis. For X-ray structural study a monocrystal with prismatic habit was chosen with linear dimensions 0.1 x 0.2 x 0.2 mm after recrystallization from ethanol. The monoclinic crystals belonged to space group $P2_1c$ with unit cell parameters: a =14.532(3), b = 8.334(3), c = 15.872(3) Å, β = 112.75(3)°, V = 1772.7 $Å^3$, d_{calc} = 1.302 g/cm^3, $C_{20}H_{17}N_3O_3$, with Z = 4. To determine and refine the structure 4454 independent reflexions with $I \geq 3\sigma(I)$ were used. The structure was determined by the direct method via the SHELX-93 suite of programs [22]. Refinement was in the anisotropic approximation for C, O, and N atoms.

Hydrogen atoms were localized by difference Fourier syntheses and refined in the isotropic approximation. GOOF(S) = 1.146, the final R factors were $R_1 = 0.054$, $wR_2 = 0.139$.

Complete X-ray crystallographic data can be obtained from F. Z. Macaev.

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