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SYNTHESIS OF FUNCTIONALLY SUBSTITUTED PYRROLO[2,3-*g*]- AND PYRROLO[3,2-*f*]QUINOLINES FROM 5-AMINO-2-PHENYL- AND 5-AMINO-1-METHYL-2-PHENYLINDOLES

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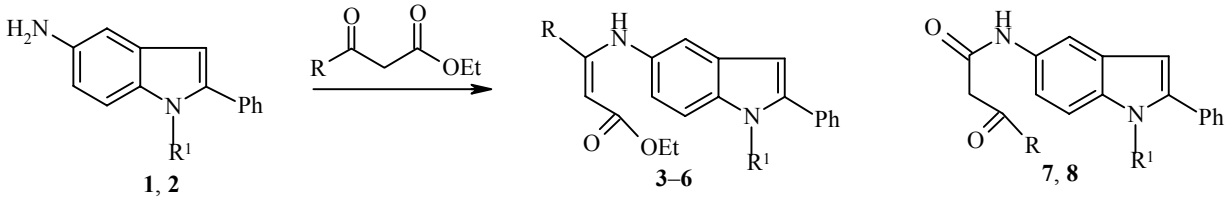
The behavior of 5-amino-2-phenyl- and 5-amino-1-methyl-2-phenylindoles in reactions with acetoacetic, trifluoroacetoacetic, and ethoxymethylenemalonic esters, leading to the preparation of pyrrolo[2,3-g]- and pyrrolo[3,2-f]quinolines with functional substituents has been studied.

Keywords: 5-amino-2-phenylindole, 5-amino-1-methyl-2-phenylindole, acetoacetic ester, trifluoroacetoacetic ester, ethoxymethylenemalonic ester, functionally substituted pyrrolo[2,3-*g*]quinolines, functionally substituted pyrrolo[3,2-*f*]quinolines.

We discovered previously that the thermal condensation of 5-amino-2-phenyl- (**1**) and 5-amino-1-methyl-2-phenylindoles (**2**) with acetylacetone and dibenzoylmethane leads to the corresponding enamino ketones which cyclize in trifluoroacetic acid into a mixture of pyrroloquinolines of angular and linear structure [1]. Wlile continuing investigations in this direction we have studied the reaction of **1** and **2** with acetoacetic, trifluoroacetoacetic, and ethoxymethylenemalonic esters with the aim of developing methods for the synthesis of functionally substituted pyrrolo[2,3-*g*]- and pyrrolo[3,2-*f*]quinolines.

It turned out that the interaction of amines **1** and **2** with the esters listed above, as in the case of 1,3-diketones, goes with the participation of only the amino group, although reaction at the β-position of the pyrrole ring is not excluded. Such reactions are known for example for derivatives of 2-aminoindole [2].

Mixtures of the *E*- and *Z*-isomers of aminocrotonates **3** and **4** are obtained on heating aminoindoles **1** and **2** with acetoacetic ester in absolute benzene with catalytic quantities of glacial acetic acid.



1, **2** **3–6** **7**, **8**

1 R^1 = H, **2** R^1 = Me, **3** R = Me, R^1 = H, **4** R = R^1 = Me, **5**, **7** R = CF_3, R^1 = H, **6**, **8** R = CF_3, R^1 = Me

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According to the integrated intensity of the signals of the characteristic protons in the ^{1}H NMR spectrum of compound **3** (Table 1) in DMSO-d_6 solution the ratio of the *Z*- and *E*-forms was 3.5:1. Assignment to the *Z*- and *E*-forms was based on the differences in chemical shift of the signals of certain protons. The signal of the N–H proton of the enamine fragment for the *Z*-form, due to interaction with the ethoxycarbonyl group, was displaced by 2 ppm towards low field compared with the signal of this proton in the *E*-form. This influence is also felt on the chemical shifts of the ethoxy group protons, the difference of which for the *Z*- and *E*-forms was 0.12 ppm. Due to the influence of the ethoxycarbonyl group the signal of the protons of the β-methyl group was displaced towards low field by 0.45 ppm in the *E*-form.

An analogous picture is also observed for indolylaminocrotonate **4**, the ratio of the *Z*- and *E*-isomers for which, according to data of ^{1}H NMR spectra, was 3:1. The results obtained are in agreement with the data of the crotonates formed with other aminoindoles previously investigated by us [3, 4].

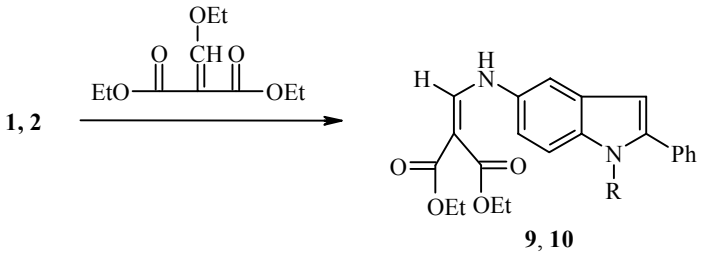
In difference to the unfluorinated analog trifluoroacetoacetic ester reacts with amines **1** and **2** under the same conditions with the participation not only of the carbonyl but also of the ethoxycarbonyl group. The corresponding *Z*-enamines **5** and **6** and amides **7** and **8** were isolated in ratios of 1:4 (**5** and **7**) and 1:3 (**6** and **8**). The corresponding enamines and amides were separated chromatographically in an aluminum oxide thin layer. In the ^{1}H NMR spectrum of indolylaminocrotonate **5** signals were observed for the protons of the ethoxy group (1.30 and 4.19), the vinylic proton (5.2), the phenyl group protons, the aromatic protons 4-, 6-, and 7-H, and the N–H group proton of the enamine (9.81 ppm) and the pyrrole fragments. The fluorinated aminocrotonate **5**, unlike the unfluorinated enamine **3**, exists exclusively in the *Z*-form, which follows from a comparison of the chemical shifts of the protons of the ethoxy group, and of the vinylic and amine protons. Analogous regularities were observed in the spectrum of indolylaminocrotonate **6**, which also indicates its *Z*-structure.

In the mass spectra of compounds **5** and **6**, apart from the molecular ion peak, there was a peak for the $[M-46]^+$ ion, which was the most intense for enamine **6**. Loss of a molecule of ethyl alcohol, characteristic of the majority of indolylaminocrotonates, leads to the formation of the molecular ion of the corresponding pyrroloquinolones **17** and **18** (see below for interpretation of structures), because the mass spectral breakdown of the latter and the further breakdown picture of enamines **5** and **6** are the same. The UV spectra of both the fluorinated and unfluorinated indolylaminocrotonates **3-6** contain the same absorption bands, which indicates the similarity of their structure.

Regretably, IR spectroscopy proved to be uninformative when studying the structure of enaminocarbonyl compounds and amides of the indole series. As was shown by us previously in [5] the band for the stretching vibrations of the conjugated carbonyl group in such systems was displayed in the area for conjugated double bond vibrations (1600-1620 cm^{-1}).

The predominant formation of amides in the reactions of aminoindoles **1** and **2** with fluorinated acetoacetic ester, unlike with acetoacetic ester itself, is probably linked with the acceptor influence of the trifluoromethyl group, which increases the reactivity of the ester grouping. Confirmation of the formation of amides **7** and **8** was the absence from their ^{1}H NMR spectra of signals for the ethoxy group protons. The number of hydrogen atoms in the molecules of the amides obtained corresponds to the total integrated intensity of the protons in the spectra. A clear assignment of the available signals was hindered by the existence in the solution (DMSO-d_6–CCl_4, 1:3) of the amides in a minimum of three forms: carbonyl, enolic, and as cyclization products. This is also confirmed by a chromatographic check. In connection with this, the amides were not characterized as individual compounds, although their molecular weights measured mass-spectrometrically corresponded to calculated values.

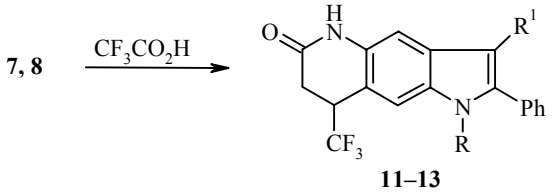
Aminoindoles **1** and **2** react with ethoxymethylenemalonic ester on boiling in ethyl alcohol with the formation of the corresponding (5-indolylaminomethylene)malonates **9** and **10**.



9 R = H, **10** R = Me

In the ^{1}H NMR spectra of malonates **9** and **10** multiplet signals were observed for the protons of the two ethoxy groups, singlet signals for the protons 1-H (**9**), CH_3 (**10**), and proton 3-H, a multiplet for the aromatic protons, and two doublets for the vinylic and amino protons of the enamine fragment with coupling constant 15 Hz, which unequivocally confirms their *anti* disposition in structures **9** and **10**.

On heating amides **7** and **8** in trifluoroacetic acid the pyrroloquinolines **11-13** are formed with linear linking of the rings.



11 R = R^1 = H, **12** R = Me, R^1 = H, **13** R = Me, R^1 = CF_3CO

The linear structure of compounds **11-13** is confirmed unequivocally by ^{1}H NMR spectra, in which singlet signals were observed for the protons at 1-H (**11**), CH_3 (**12, 13**), 3-H (**11, 12**), 4-, 7-, and 9-H. The picture of an ABC system for the protons of the phenyl group for compound **13** differed somewhat from the remainder (two triplet signals are in superimposition), seemingly due to the influence of the trifluoroacetyl group located close to it. The trifluoroacetyl group also displaces the 4-H proton signal towards low field by 0.77 ppm. The structure of compound **13** is also confirmed by the mass spectrum in which there is a peak for the molecular ion and the most intense peak in the spectrum is for the $[M\text{-}69]^+$ ion. This character of the mass spectral decomposition is explained by the presence in the molecule of the trifluoroacetyl group [6].

Amides of 5-indolyltrifluoroacetic acid under conditions of acid catalysis even with a free position of the β pyrrole ring are cyclized with the participation of position 6 and not 4, which leads to a linearly constructed pyrroloquinoline, unlike the same nonfluorinated amides which are converted under analogous conditions predominantly into pyrroloquinolines of angular structure [3]. Such an anomaly must probably be explained by the large steric requirements of the trifluoromethyl group compared with methyl. The *peri* substituents (methyl and hydrogen) do not create stress in the angular pyrroloquinoline and the formation of the latter with a trifluoromethyl group and hydrogen in the *peri* positions is found to be difficult.

Under the action of dimethyl sulfate compounds **11** and **12** are readily converted into pyrroloquinoline **14** methylated at both nitrogen atoms.

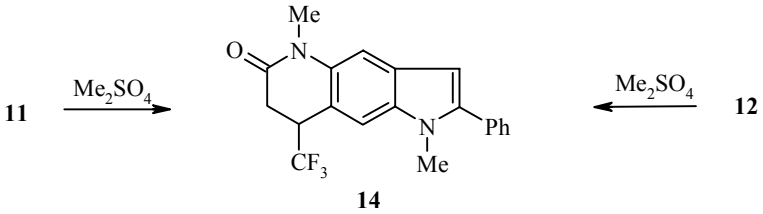


TABLE 1. Physicochemical and Spectral Characteristics of the Compounds Obtained

Compound	Empirical foprmula	Found, % / Calculated, %			R_f (system)	mp, °C (solvent)	^{1}H NMR spectrum, δ, ppm (*J*, Hz)	UV spectrum		Yield, %
		C	H	M^+				λ_{max}, nm	log ε	
1	2	3	4	5	6	7	8	9	10	11
3	$C_{20}H_{20}N_2O_2$	74.75 / 74.98	6.12 / 6.29	320 / 320	0.71 (C)	160-162 (light petroleum)	(*E*) 1.13 (3H, t, *J* = 7, $OCH_2\underline{CH_3}$); 2.37 (3H, s, α-CH_3); 3.90 (2H, q, *J* = 7, $O\underline{CH_2}CH_3$); 4.75 (1H, s, H vin.); 6.78 (1H, s, 3-H); 7.45 (8H, m, 4-, 6-, 7-H, Ph); 8.07 (1H, s, N–H amin.); 11.36 (1H, s, 1-H) (*Z*) 1.25 (3H, t, *J* = 7, $OCH_2\underline{CH_3}$); 1.93 (3H, s, α-CH_3); 4.07 (2H, q, *J* = 7, $O\underline{CH_2}CH_3$); 4.57 (1H, s, H vin.); 6.78 (1H, s, 3-H); 7.45 (8H, m, 4-, 6-, 7-H, Ph); 10.23 (1H, s, N–H amin.); 11.40 (1H, s, 1-H)	210 225 350	4.19 4.32 4.48	58
4	$C_{21}H_{22}N_2O_2$	75.28 / 75.42	6.75 / 6.63	334 / 334	0.84 (C)	139-141 (light petroleum)	(*E*) 1.13 (3H, t, *J* = 7, O–$CH_2\underline{CH_3}$); 2.38 (3H, s, α-CH_3); 3.77 (3H, s, 1-CH_3); 3.93 (2H, q, *J* = 7, O–$\underline{CH_2}CH_3$); 4.75 (1H, s, H vin.); 6.50 (1H, s, 3-H); 7.28 (8H, m, 4-, 6-, 7-H, Ph); 8.09 (1H, s, N–H amin.) (*Z*) 1.26 (3H, t, *J* = 7, O–$CH_2\underline{CH_3}$); 1.93 (3H, s, α-CH_3); 3.77 (3H, s, 1-CH_3); 4.10 (2H, q, *J* = 7, $O\underline{CH_2}CH_3$); 4.58 (1H, s, H vin.); 6.50 (1H, s, 3-H); 7.27 (8H, m, 4-, 6-, 7-H, Ph); 10.26 (1H, s, N–H amin.)			
5	$C_{20}H_{17}F_3N_2O_2$	64.26 / 64.17	4.41 / 4.58	374 / 374	0.82 (B)	175-176 (heptane)	(*Z*) 1.30 (3H, t, *J* = 7, OCH_2–$\underline{CH_3}$); 4.19 (2H, q, *J* = 7, O–$\underline{CH_2}CH_3$); 5.20 (1H, s, H vin.); 6.74 (1H, s, 3-H); 6.93 (1H, d, *J* = 8, 7-H); 7.28 (1H, t, *J* = 8, *p*-H, Ph); 7.35 (1H, s, 4-H); 7.35 (1H, d, *J* = 8, 6-H); 7.41 (2H, t, *m*-H, Ph); 7.80 (2H, d, *o*-H, Ph); 9.81 (1H, s, N–H amin.); 11.42 (1H, s, 1-H)	210 230 315	4.47 4.37 4.58	15*

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11
6	$C_{21}H_{19}F_3N_2O_2$	64.71 64.94	4.70 4.93	388 388	0.71 (A)	128-129 (heptane)	(*Z*) 1.33 (3H, t, *J* = 7, O–CH$_2$C<u>H$_3$</u>); 3.80 (3H, s, 1-CH$_3$); 4.20 (2H, q, *J* = 7, O<u>CH$_2$</u>–CH$_3$); 5.22 (1H, s, H vin.); 6.48 (1H, s, 3-H); 7.04 (1H, d, *J* = 8, 7-H); 7.36 (1H, d, *J* = 8, 6-H); 7.40 (1H, s, 4-H); 7.40 (1H, t, *J* = 8, *p*-H, Ph); 7.48 (2H, t, *J* = 8, *m*-H, Ph); 7.53 (2H, d, *J* = 8, *o*-H, Ph); 9.83 (1H, s, N–H amin.)	210 225 300	4.36 4.40 4.50	13*[2]
9	$C_{22}H_{22}N_2O_4$	69.90 69.83	5.61 5.86	378 378	0.46 (B)	163-164	1.30 (6H, m, 2 OCH$_2$C<u>H$_3$</u>); 4.21 (4H, m, 2 O<u>CH$_2$</u>CH$_3$); 6.89 (1H, s, 3-H); 7.38 (8H, m, 4-, 6-, 7-H, Ph); 8.44 (1H, d, *J* = 15, H vin.); 10.77 (1H, d, *J* = 15, H amin.); 11.49 (1H, s, 1-H)	207 227 333	4.37 4.30 4.51	43
10	$C_{23}H_{24}N_2O_4$	70.21 70.39	6.31 6.16	392 392	0.59 (C)	106-108	1.33 (6H, m, 2 OCH$_2$C<u>H$_3$</u>); 3.77 (3H, s, 1-CH$_3$); 4.22 (4H, m, 2 O<u>CH$_2$</u>CH$_3$); 6.53 (1H, s, 3-H); 7.34 (8H, m, 4-, 6-, 7-H, Ph); 8.46 (1H, d, *J* = 15, H vin.); 10.92 (1H, d, *J* = 15, N–H amin.)	208 225 320	4.57 4.54 4.65	66
11	$C_{18}H_{11}F_3N_2O$	65.92 65.86	3.21 3.38	328 328	0.41 (D)	> 300	6.73 (1H, s, 3-H); 6.84 (1-H, s, 7-H); 7.33 (1H, t, *J* = 8, *p*-H, Ph); 7.45 (2H, t, *J* = 8, *m*-H, Ph); 7.52 (1H, s, 4-H); 7.76 (1H, s, 9-H); 7.84 (2H, d, *J* = 8, *o*-H, Ph); 11.48 (1H, s, 1-H); 11.80 (1H, s, 5-H)			
12	$C_{19}H_{13}F_3N_2O$	66.45 66.67	3.76 3.83	342 342	0.42 (F)	282-283 (aq. alcohol)	3.84 (3H, s, 1-H); 6.55 (1H, s, 3-H); 6.77 (1H, s, 7-H); 7.45 (1H, t, *J* = 8, *p*-H, Ph); 7.51 (2H, t, *J* = 8, *m*-H, Ph); 7.56 (1H, s, 4-H); 7.58 (2H, d, *J* = 8, *o*-H, Ph); 7.64 (1H, s, 9-H); 11.93 (1H, s, 1-H)	230 250 364	4.61 4.70 4.52	28
13	$C_{21}H_{12}F_6N_2O_2$	57.30 57.54	2.85 2.76	438 438	0.68 (G)	> 300 (alcohol)	3.65 (3H, s, 1-H); 6.86 (1H, s, 7-H); 7.48 (2H, d, *o*-H, Ph); 7.57 (3H, m, *m*-, *p*-H, Ph); 7.74 (1H, s, 9-H); 8.33 (1H, s, 4-H); 12.14 (1H, s, 5-H)	220 238 272 (sh) 317 330	4.51 4.43 3.39 4.35 4.18	22
14	$C_{20}H_{15}F_3N_2O$	67.26 67.41	4.10 4.24	356 356	0.74 (G)	263-264 (alcohol)	3.75 (3H, s, 5-CH$_3$); 3.86 (3H, s, 1-CH$_3$); 6.68 (1H, s, 3-H); 6.89 (1H, s, 7-H); 7.47 (1H, t, *J* = 8, *p*-H, Ph); 7.53 (2H, t, *J* = 8, *m*-H, Ph); 7.59 (2H, d, *J* = 8, *o*-H, Ph); 7.67 (1H, s, 4-H); 7.71 (1H, s, 9-H)	230 250 356	4.51 4.60 4.41	56
15	$C_{18}H_{14}N_2O$	78.65 78.81	5.21 5.14	274 274	0.63 (J)	>300 (alcohol)	2.37 (3H, s, 7-CH$_3$); 5.93 (1H, s, 8-H); 7.24 (1H, d, *J* = 8, 4-H); 7.30 (1H, t, *J* = 8, *p*-H, Ph); 7.46 (2H, t, *J* = 8, *m*-H, Ph); 7.66 (1H, d, *J* = 8, 5-H); 7.86 (2H, d, *o*-H, Ph); 7.90 (1H, s, 1-H); 11.35 (1H, s, 6-H); 11.71 (1H, s, 3-H)	207, 230 252 (sh) 301 360	4.32 4.36 4.11 4.15 4.23	58

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11
16	$C_{19}H_{16}N_2O$	79.21 79.14	5.45 5.59	288 288	0.61 (J)	228-230 (alcohol)	2.37 (3H, s, 7-CH_3); 3.85 (3H, s, 3-CH_3); 5.93 (1H, s, 8-H); 7.32 (1H, d, *J* = 8, 4-H); 7.43 (1H, t, *J* = 8, *p*-H, Ph); 7.52 (2H, t, *J* = 8, *m*-H, Ph); 7.61 (2H, d, *J* = 8, *o*-H Ph); 7.69 (1H, s, 1-H); 7.77 (1H, d, *J* = 8, 5-H); 11.36 (1H, s, 6-H)	208 223 254 294 345	4.46 4.45 4.26 4.18 4.26	43
17	$C_{18}H_{11}F_3N_2O$	65.38 65.86	3.42 3.38	328 328	0.44 (E)	>300 (alcohol)	7.19 (1H, s, 8-H); 7.26 (1H, t, *J* = 8, *p*-H, Ph); 7.43 (2H, t, *J* = 8, *m*-H, Ph); 7.64 (1H, d, *J* = 8, 4-H); 7.71 (1H, s, 1-H); 7.86 (1H, d, *J* = 8, 5-H); 7.89 (2H, d, *J* = 8, *o*-H, Ph); 11.40 (1H, s, 6-H); 11.90 (1H, s, 3-H)	209 226 280 350	4.40 4.29 4.14 4.10	80
18	$C_{19}H_{13}F_3N_2O$	66.38 66.67	3.75 3.83	342 342	0.69 (E)	282-283 (aq. alcohol)	3.97 (3H, s, 3-CH_3); 7.22 (1H, s, 8-H); 7.40 (1H, t, *J* = 8, *p*-H, Ph); 7.45 (1H, s, 1-H); 7.50 (2H, t, *J* = 8, *m*-H, Ph); 7.61 (2H, d, *J* = 8, *o*-H, Ph); 7.76 (1H, d, *J* = 8, 4-H); 7.91 (1H, d, *J* = 8, 5-H); 11.43 (1H, s, 6-H)	210 227 274 345	4.42 4.39 4.37 4.18	93
19	$C_{20}H_{16}N_2O_3$	71.95 72.28	4.96 4.85	332 332	0.38 (K)	>300 (alcohol)	1.31 (3H, t, *J* = 7, $OCH_2\underline{CH_3}$); 4.28 (2H, q, *J* = 7, $O\underline{CH_2}CH_3$); 7.36 (1H, d, *J* = 8, 4-H); 7.60 (5H, m, *o*-H, Ph); 7.80 (1H, d, *J* = 8, 5-H); 8.04 (1H, s, 1-H); 8.44 (1H, s, 7-H); 11.90 (1H, s, 3-H); 12.25 (1H, s, 9-OH)	207 228 276 (sh) 303 370	4.24 4.23 4.05 4.10 4.03	56
20	$C_{21}H_{18}N_2O_3$	72.61 72.82	5.31 5.24	346 346	0.20 (H)	263-265 (alcohol)	1.32 (3H, t, *J* = 7, $OCH_2\underline{CH_3}$); 3.87 (3H, s, 3-CH_3); 4.26 (2H, q, *J* = 7, $O\underline{CH_2}CH_3$); 7.41 (1H, d, *J* = 8, 4-H); 7.46 (1H, t, *J* = 8, *p*-H, Ph); 7.54 (2H, t, *J* = 8, *m*-H, Ph); 7.63 (2H, d, *J* = 8, *o*-H, Ph); 7.73 (1H, s, 1-H); 7.88 (1H, d, *J* = 8, 5-H); 8.43 (1H, s, 7-H); 12.15 (1H, s, 9-OH)	206 227 267 303 357	4.23 4.32 4.04 4.23 4.18	48

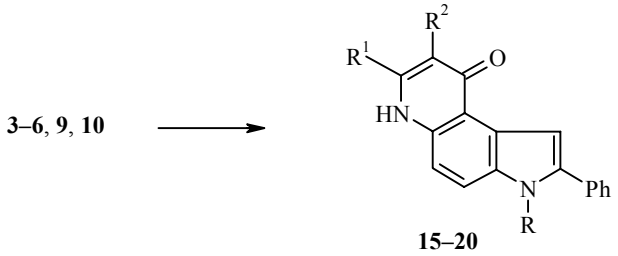
* Overall yield of enamine and amide was 82%.

*[2] Overall yield of enamine and amide was 56%.

The ^{1}H NMR spectrum of compound **14** differs from the spectra of pyrroloquinolines **11** and **12** by the absence of the N–H signals and by the presence of two singlet signals for the protons of the N-methyl groups. The UV spectra of pyrroloquinolines **11**, **12**, and **14** are characterized by four absorption bands and are practically identical.

Compound **13** is formed together with pyrroloquinoline **12** by acylation of the latter in the β-position of the pyrrole ring with trifluoroacetic acid. The nucleophilicity of the β-position is probably somewhat increased due to the presence of the methyl group.

High temperature (250-280°C) cyclization of indolylaminocrotonates **3-6** and indolylmethylene-malonates **9**, **10** leads to pyrroloquinolines **15-20** of angular structure.



15–20

15 R = R^2 = H, R^1 = Me, **16** R = R^1 = Me, R^2 = H, **17** R = R^2 = H, R^1 = CF_3;
18 R = Me, R^2 = H, R^1 = CF_3, **19** R = R^1 = H, R^2 = CO_2Et, **20** R = Me, R^1 = H, R^2 = CO_2Et

On boiling compounds **3** and **4** in biphenyl the pyrroloquinolines **15** and **16** are formed, the product of the alternative cyclization at position 6 was not detected. The angular connection of the rings in compounds **15** and **16** is confirmed by the presence in the ^{1}H NMR spectra of two doublets for the 4-H and 5-H protons (J = 8 Hz) and also the low field position of the signal for the 1-H proton (for compound **15**), found in the position *peri* to the γ-oxygen atom of the pyridone ring. Pyrroloquinolines **15** and **16** are stable towards electron impact, consequently the most intense peaks in their mass spectra are the molecular ions with *m/z* 274 and 288 respectively. The presence of peaks for $[M\text{-}CO]^+$ ions points in favor of a γ-quinolone structure for the compounds. The UV spectra of compounds **15** and **16** are practically identical, which confirms their similar structure.

Like crotonates **3** and **4** their fluorinated analogs **5** and **6** are converted on boiling in biphenyl into the corresponding trifluoromethyl-substituted angular pyrroloquinolines **17** and **18**. The same regularities are observed in the spectral characteristics as for compounds **15** and **16**.

Thermal cyclization of indolylmalonates in dowtherm (250°C) also leads to the formation of angular pyrroloquinolines **19** and **20**. This is confirmed by the presence in the ^{1}H NMR spectra of the obtained compounds of signals for the protons of the ethoxy group, singlet signals for the 3-H protons (compound **19**), 3-CH_3 (compound **20**), and the 1-, 7-H, and 9-OH protons. Unlike compounds **15-18** pyrroloquinolines **19** and **20** are in the γ-hydroxyquinoline form, which was confirmed by the presence of a singlet signal for the α-pyridine proton (7-H), and also by the character of the mass spectral decomposition. In the mass spectra of pyrroloquinolines **19** and **20** the most intense signal was the $[M\text{-}46]^+$ peak, which corresponds to elimination of a molecule of alcohol from the molecular ion. Such fragmentation is characteristic for *o*-ethoxycarbonylphenols.

EXPERIMENTAL

The NMR spectra were recorded on Bruker DRX-500 (500 MHz) and Bruker AM-300 (300 MHz) instruments in DMSO-d_6 (compounds **3**, **4**, **9**, **10**, **15**, **16**, **19**, **20**) and DMSO-d_6–CCl_4, 1:3 (compounds **5-8**, **11-14**, **17**, **18**), internal standard was TMS. The mass spectra were obtained on a Finnigan MAT INCOS-50

mass spectrometer with direct insertion of samples into the ion source at an ionization energy of 70 eV. Electronic spectra were recorded on a Specord spectrophotometer in ethanol. Purification of reaction products was carried out by column chromatography, and also preparatively on Al_2O_3 plates (neutral, Brockmann grade I and II). A check on the course of reactions and the purity of the compounds obtained was effected by TLC on Silufol UV-254 plates in the systems benzene (A), benzene–ethyl acetate, 8:1 (B), 5:1 (C), 3:2 (D), 3:1 (E), 1:1 (F), 2:1 (G), ethyl acetate (H), ethyl acetate–methanol, 5:2 (I), 3:1 (J), and 5:1 (K).

The physicochemical and spectral characteristics of the compounds obtained are given in Table 1. The preparation of the initial aminoindoles **1** and **2** is described in [1].

Ethyl Ester of (*E,Z*)-3-[(2-Phenyl-1H-5-indolyl)amino]crotonic Acid (3). A solution of 5-amino-2-phenylindole **1** (0.57 g, 2.74 mmol) and acetoacetic ester (0.3579 g, 2.75 mmol) in absolute benzene (100 ml) in the presence of traces of glacial acetic acid was heated for 28 h with a Dean–Stark apparatus. At the end of the reaction (check by TLC) the benzene was distilled off. The compound obtained was purified by passing a boiling benzene solution through a layer (2-3 cm) of aluminum oxide. Yield 0.51 g.

Ethyl Ester of (*E,Z*)-3-[(1-Methyl-2-phenyl-1H-5-indolyl)amino]crotonic Acid (4) was obtained analogously from 5-amino-1-methyl-2-phenylindole (**2**) (1.04 g, 4.68 mmol) and acetoacetic ester (0.634 g, 4.88 mmol), heating for 19-20 h. Yield 0.8 g.

Ethyl Ester of 4,4,4-Trifluoro-3-[(2-phenyl-1H-5-indolyl)amino]crotonic Acid (5) and N-(2-Phenyl-1H-5-indolyl)amide of 4,4,4-Trifluoro-3-oxobutyric Acid (7). A solution of compound **1** (0.79 g, 3.8 mmol) and trifluoroacetoacetic ester (0.85 g, 4.62 mmol) in absolute benzene was boiled in the presence of catalytic amounts of glacial acetic acid for 40 h (chromatographic control) with a Dean–Stark apparatus. The benzene was distilled off at the end of the reaction. The solid residue (a mixture of enamine **5** and amide **7**) of weight 1.233 g was boiled in heptane. The hot solution of enamine **5** was filtered from the undissolved solid and passed through a layer (1 cm) of aluminum oxide. Yield was 0.22 g. The solid not dissolving in heptane is amide **7** (yield 0.874 g), purified by recrystallization from alcohol with active carbon. The compound obtained was not homogeneous according to chromatographic analysis. The overall integrated intensity of protons in the ^{1}H NMR spectrum corresponds to the amide structure. Mass spectrum: found 346 $[M]^+$; calculated: M = 346.

Ethyl Ester of 4,4,4-Trifluoro-3-[(1-methyl-2-phenyl-1H-5-indolyl)aminocrotonic Acid (6) and N-(1-Methyl-2-phenyl-1H-5-indolyl)amide of 4,4,4-Trifluoro-3-oxobutyric Acid (8) were obtained analogously from compound **2** (1.14 g, 5.14 mmol) and trifluoroacetoacetic ester (1.1 g, 5.98 mmol) but heating was carried out for 50 h. Aminocrotonate **6** was purified by passing a boiling solution in a mixture of hexane and benzene through a layer (1 cm) of aluminum oxide. Yield 0.265 g. The solid insoluble in heptane was amide **8**. The substance was purified by passing a boiling solution in a mixture of benzene and heptane through a layer (1 cm) of aluminum oxide. Recrystallization was from heptane. Yield was 0.68 g. The overall integrated intensity of protons in the ^{1}H NMR spectrum corresponded to the amide structure. Mass spectrum: found 360 $[M]^+$; calculated: M = 360.

Diethyl Ester of 2-[(2-Phenyl-1H-5-indolyl)aminomethylene]malonic Acid (9). A mixture of compound **1** (0.468 g, 2.25 mmol) and ethoxymethylenemalonic ester (0.52 g, 2.4 mmol) in ethyl alcohol (5 ml) was boiled for 1 h 30 min. The solid precipitated after cooling was filtered off, and washed with cold alcohol. Yield 0.37 g.

Diethyl Ester of 2-[(1-Methyl-2-phenyl-1H-5-indolyl)aminomethylene]malonic Acid (10) was obtained analogously from compound **2** (0.5 g, 2.25 mmol) and ethoxymethylenemalonic ester (0.52 g, 2.4 mmol). Yield 0.58 g.

2-Phenyl-8-trifluoromethyl-5,6-dihydro-1H-pyrrolo[2,3-*g*]quinol-6-one (11). Amide **7** (0.3 g, 0.87 mmol) was boiled in trifluoroacetic acid (5 ml) for 3 h. The reaction mass was then poured into 12% aqueous ammonia with ice. The precipitated solid was filtered off and washed many times with water. The substance was purified in a binder-free thick layer of aluminum oxide in ethyl acetate. Yield 0.216 g.

1-Methyl-2-phenyl-8-trifluoromethyl-5,6-dihydro-1H-pyrrolo[2,3-*g*]quinol-6-one (12) and 1-Methyl-2-phenyl-3-trifluoroacetyl-8-trifluoromethyl-5,6-dihydro-1H-pyrrolo[2,3-*g*]quinol-6-one (13) were obtained analogously from amide **8** (0.292 g, 0.811 mmol), but heating was carried out for 5 h. The obtained mixture of substances **12** and **13** was separated in a binder-free thick layer of aluminum oxide in the system benzene–ethyl acetate, 1:2. Yield of pyrroloquinoline **12** 0.077 g. Yield of pyrroloquinoline **13** 0.077 g.

1,5-Dimethyl-2-phenyl-8-trifluoromethyl-5,6-dihydro-1H-pyrrolo[2,3-*g*]quinol-6-one (14). A. A solution of pyrroloquinoline **11** (0.15 g, 0.457 mmol) and an excess of dimethyl sulfate and potassium hydroxide in acetone was heated for 1 h. At the end of the reaction the acetone was distilled off, and the reaction mass diluted with water. The precipitated solid was filtered off. Yield 0.09 g.

B. Compound **14** was obtained analogously from pyrroloquinoline **12**, heating for 2 h.

7-Methyl-2-phenyl-6,9-dihydro-3H-pyrrolo[3,2-*f*]quinol-9-one (15). Aminocrotonate **3** (0.64 g, 2 mmol) in biphenyl was boiled for 30 min. The cooled reaction mixture was poured into petroleum ether. The precipitated solid was filtered off, and washed with hot hexane. Yield 0.32 g.

3,7-Dimethyl-2-phenyl-6,9-dihydro-3H-pyrrolo[3,2-*f*]quinol-9-one (16) was obtained analogously from aminocrotonate **4** (0.67 g, 2 mmol). Yield 0.25 g.

2-Phenyl-7-trifluoromethyl-6,9-dihydro-3H-pyrrolo[3,2-*f*]quinol-9-one (17) was obtained analogously from aminocrotonate **5** (0.188 g, 0.503 mmol) heating for 15 min. Yield 0.133 g. The substance obtained was purified in a binder-free thick layer of aluminum oxide in a mixture of benzene–ethyl acetate, 3:1.

3-Methyl-2-phenyl-7-trifluoromethyl-6,9-dihydro-3H-pyrrolo[3,2-*f*]quinol-9-one (18) was obtained analogously from aminocrotonate **6** (0.13 g, 0.335 mmol). Yield 0.103 g.

Ethyl Ester of 9-Hydroxy-2-phenyl-3H-pyrrolo[3,2-*f*]quinoline-8-carboxylic Acid (19). A solution of aminomethylenemalonate **9** (0.57 g, 1.5 mmol) in dowtherm was boiled for 30 min. The cooled reaction mixture was poured into petroleum ether. The precipitated solid was filtered off, and washed many times with hot hexane. Pyrroloquinoline **19** (0.28 g) was isolated.

Ethyl Ester of 9-Hydroxy-3-methyl-2-phenyl-3H-pyrrolo[3,2-*f*]quinoline-8-carboxylic Acid (20) was obtained analogously from aminomethylenemalonate **10** (0.59 g, 1.5 mmol). Yield 0.25 g.

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