J_{45} = 9 Hz), and 7.57 ppm (d, 5-H, J_{54} = 9 Hz) [the ratio of the integral intensity of 4-H (VIIb) to that of 4-H (VIIa) was 1.2:1].

Pyrroloquinolone Va was separated from isomer Vb by repeated crystallization from ethanol. Compounds Vb, VIIa, and VIIb were not isolated in individual form.

C) A solution of 2 mmole of the aminocrotonate in trifluoroacetic acid was heated in a sealed ampul at 150°C for 2-3 h. The pyrroloquinolones were isolated by a method similar to that described in [2].

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SYNTHESIS OF 2-ARYL-4-METHYL-9H-INDOLO[2,3-f]QUINOLINES

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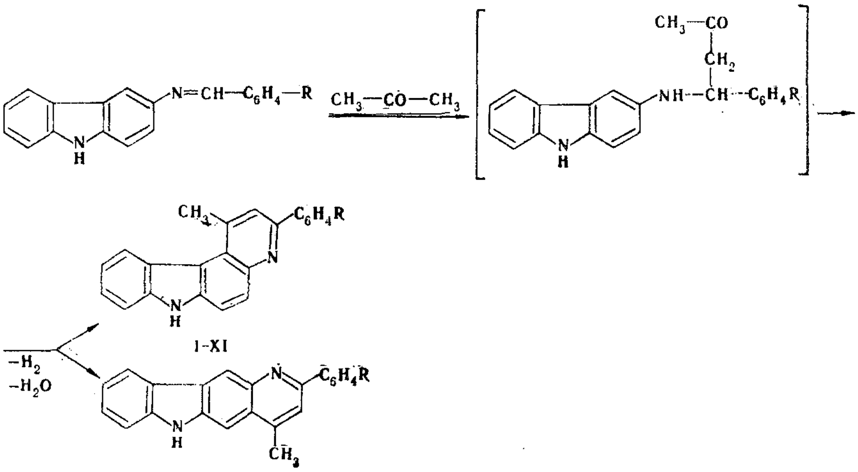
A new series of indoloquinoline derivatives was obtained by catalytic condensation of carbazole-containing azomethines with acetone. It was shown by means of a combination of physicochemical methods of investigation (UV, IR, NMR, and mass spectroscopy) that the synthesized compounds have angular structures.

We have previously demonstrated the possibility of the synthesis of 2,4-diaryl- and 2-aryl-4-styryl-9H-indolo[2,3-f]quinolines on the basis of carbazole-containing azomethines [1, 2]. 2-Aryl-4-methyl-9H-indolo[2,3-f]quinolines were obtained by the reaction of azomethines of the carbazole series with acetone. The formation of these compounds evidently takes place via the scheme



I R=H; II R=*p*-Cl; III R=*p*-Br; IV R=*p*-F; V R=*p*-NO_2; VI R=*m*-Br; VII R=*m*-Cl; VIII R=*m*-I; IX R=*m*-F; X R=*o*-F; XI R=*p*-OCH_3

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	R_f/R_{f_1}	Found, %			Empirical formula	Calc., %			M^+	Yield, %
			C	H	N		C	H	N		
I	227—228	1,00	85,61	5,27	9,22	$C_{22}H_{16}N_2$	85,72	5,19	9,09	308	28
II	235—236	1,43	77,30	4,25	8,22	$C_{22}H_{15}ClN_2$	77,19	4,39	8,19	342/344	42
III	229—230	1,52	68,24	3,96	7,36	$C_{22}H_{15}BrN_2$	68,39	3,89	7,25	386/388	45
IV	192—193	1,19	80,79	4,75	8,63	$C_{22}H_{15}FN_2$	80,98	4,60	8,59	326	40
V	266—267	1,38	74,59	4,38	11,75	$C_{22}H_{15}N_3O_2$	74,79	4,25	11,90	353	51
VI	194—195	1,57	68,24	3,97	7,34	$C_{22}H_{15}BrN_2$	68,39	3,89	7,25	386/388	43
VII	190—191	1,48	77,03	4,58	8,24	$C_{22}H_{15}ClN_2$	77,19	4,39	8,19	342/344	34
VIII	180—181	1,52	60,69	3,59	6,61	$C_{22}H_{15}IN_2$	60,83	3,46	6,45	434	46
IX	199—200	1,38	80,79	4,73	8,68	$C_{22}H_{15}FN_2$	80,98	4,60	8,59	326	24
X	192—193	1,14	80,91	4,78	8,67	$C_{22}H_{15}FN_2$	80,98	4,60	8,59	326	37
XI	227—228	0,48	81,51	5,21	8,42	$C_{23}H_{18}N_2O$	81,66	5,33	8,28	338	25

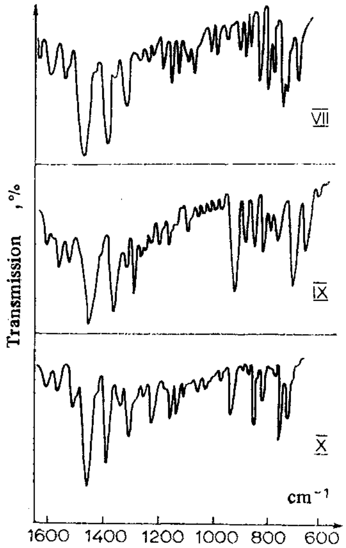

Fig. 1. IR spectra of VII, IX, and X.

The formation of two types of products, viz., compounds with linear and angular structures, is possible in this case.

As a result of these reactions, we isolated yellow-green crystalline products with high melting points that were quite soluble in dimethylformamide, dimethyl sulfoxide, and dioxane, slightly soluble in benzene, alcohol, acetone, and acetonitrile, and insoluble in water. According to the physicochemical characteristics (Table 1), the isolated compounds are individual substances.

To solve the problem of the structure of the compounds obtained we investigated the UV, IR, PMR, and mass spectra. A shift of the absorption maxima with λ from 280-295 nm to 290-305 nm and from 335-355 nm to 365-415 nm is observed in the UV spectra of all of the isolated compounds as compared with the starting azomethines. This indicates an increase in the degree of aromatic character of the synthesized compounds.

The mass spectra of I, II, and VI contain maximally intense molecular-ion peaks (M^+), and peaks of doubly charged molecular and fragment ions are also present. High intensities of the molecular-ion peaks, the presence of doubly charged ions, and a relatively small number of fragment-ion peaks in the mass spectra are characteristic for compounds with aromatic structures, and this confirms the condensed structure of the investigated compounds [3, 4]. The peak of an $[M - CH_3]^+$ ion, the development of which is due to the presence of a methyl group in the indololepidine molecule, is characteristic in the mass spectra.

An intense absorption band at 800-860 cm^{-1} is present in the IR spectra of I-XI. In the absence of a substituent in the para position of the phenyl ring (which gives a strong band in the same range) this signal makes it possible to assume the presence in the investigated compounds of a 1,2,3,4-substituted benzene ring, which is possible only in an angular structure.

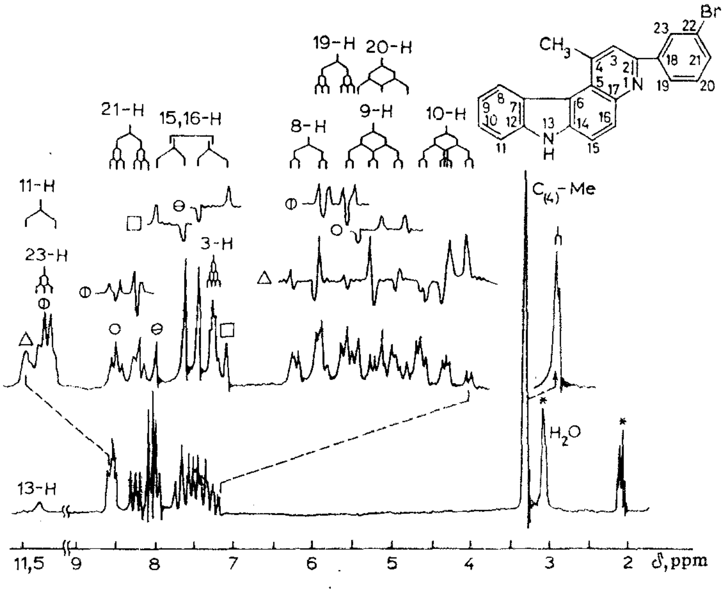

Fig. 2. PMR spectrum of VI.

The IR spectra of a number of compounds with ortho and meta substituents in the aryl part of the molecule are presented in Fig. 1. The intense absorption band near 830 cm^{-1} evidently corresponds to the vibrations of two adjacent hydrogen atoms of the aromatic carbazole ring, while the absorption bands at 860-900 cm^{-1} characterize the vibrations of the isolated hydrogen atom of different rings [5, 6]. All of this makes it possible to assume that the synthesized compounds have angular structures.

Signals of protons of an indole fragment, four protons of a bromophenyl group, and protons of the $CH_3-\underset{|}{C}=\underset{\underset{H}{|}}{C}-$ fragment and an AB quartet at 8.08 ppm, which was assigned to the 15-H and 16-H protons, are observed in the NMR spectrum of VI (Fig. 2). The presence of the AB quartet in the spectrum also confirms fusion of the angular type in the synthesized compounds.

Thus 11 new indoloquinoline derivatives were synthesized by catalytic condensation of carbazole-containing azomethines with acetone. It was established by physicochemical methods that they have angular structures, i.e., they are 2-aryl-4-methyl-9H-indolo[2,3-f]quinolines.

EXPERIMENTAL

The UV spectra of solutions of the compounds in methanol [$c = (2-4)\cdot 10^{-5}$ mole/liter] were recorded with an SF-4A spectrophotometer. The mass spectra were recorded with an LKB 2091 spectrometer with direct introduction of the samples into the ion source at 70 eV and at vaporization temperatures ranging from 80 to 200°C. The PMR spectrum of a solution of VI in deuteroacetone (SIC, Switzerland) was obtained with a Varian HA-100D spectrometer with tetramethylsilane as the internal standard; the spectrum was recorded at 32°C. The individuality of the compounds was monitored by thin-layer chromatography (TLC) on Silufol plates with acetone—benzene (1:30) as the mobile phase; the R_f values were reckoned with respect to the R_f value of unsubstituted indoloquinoline (I), the mobility of which we arbitrarily assumed to be unity.

2-Aryl-4-methyl-9H-indolo[2,3-f]quinolines. A reaction mixture consisting of equimolar amounts (0.003 mole) of the arylidene-3-aminocarbazole, nitrobenzene, 0.02 mole of acetone, 4-8 ml of ethanol, and 0.4-0.8 ml of concentrated HCl was heated in a flask equipped with a reflux condenser on a boiling-water bath for 3-4 h, after which it was cooled, and the resulting precipitate was removed by filtration, washed with alcohol, treated with ammonium hydroxide, dried, and recrystallized twice from alcohol—benzene (1:1).

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SYNTHESIS OF OPTICALLY ACTIVE 1,2,5-TRIMETHYL-4-ETHYNYL-4-PIPERIDOLS AND THE CORRESPONDING DIACETYLENIC GLYCOLS

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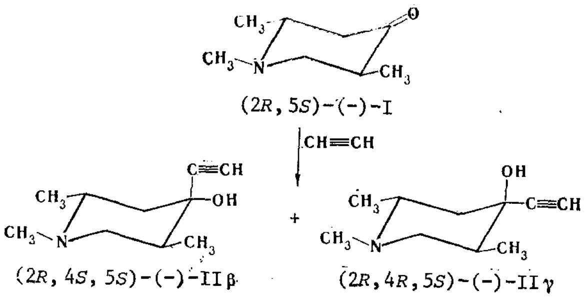
The following optically active enantiomeric pairs were synthesized by the Favorskii reaction from (+)-(2S,5R)- and (−)-(2R,5S)-trans-1,2,5-trimethyl-4-piperidones: (+)-(2S,4R,5R)- and (−)-(2R,4S,5S)-trans-1,2,5-trimethyl-4-ethynyl-4-piperidol and (+)-(2S,4S,5R)- and (−)-(2R,4R,5S)-trans-1,2,5-trimethyl-4-ethynyl-4-piperidol. Optically active 1,4-bis(1,2,5-trimethyl-4-hydroxy-4-piperidyl)buta-1,3-diynes were obtained by Glaser oxidative dimerization of the enantiomeric pairs of ethynylpiperidols. The antagonistic action of the dihydrochlorides of (+)-(2S,4R,5R)- and (−)-1,4-bis[(2R,4S,5S)-1,2,5-trimethyl-4-hydroxy-4-piperidyl]buta-1,3-diyne on cell respiration was established from the results of biological tests on cultures of tobacco and chlorella cells.

It has been previously shown that racemic diacetylenic glycols of the piperidone series obtained from trans-1,2,5-trimethyl-4a-ethynyl-4-piperidol (isomer IIβ) and trans-1,2,5-trimethyl-4e-ethynyl-4-piperidol (isomer IIγ) stimulate plant growth and that 1,4-bis(trans-1,2,5-trimethyl-4a-hydroxy-4-piperidyl)buta-1,2-diyne (IIIγ) has greater activity than glycol IIIβ [1].



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