N-Methyl-N^1-(α-methyl-β-carbethoxyvinyl)iminopyrrolidine (VII). A mixture of 6.1 g (61.6 mmole) of acetal IV and 7.95 g (61.7 mmole) of ester I was refluxed for 3 h, after which the alcohol was evaporated, and the residue was fractionated.

2-Dimethylamino-6-methyl-4-pyridone (XII) Hydrochloride. A 10.3-g sample of III was heated in the presence of catalytic amounts of p-toluenesulfonic acid at 220° for 1.5 h with removal of the alcohol by distillation. The mixture was then dissolved in acetone, an alcohol solution of HCl was added, and the mixture was filtered. PMR spectrum (δ, ppm): 2.50 (6-CH$_3$), 3.22 [N(CH$_3$)$_2$], 6.14 (3-CH), and 6.30 (5-CH) (CD$_3$OD).

1,7-Dimethyl-5-oxo-1,2,3,4,5,8-hexahydro-1,8-naphthyridine (XI). A 27.58-g (0.123 mole) sample of VIII was heated in the presence of p-toluenesulfonic acid at 220° for 30 min with removal of the alcohol by distillation. The mixture was then triturated with hexane and filtered. PMR spectrum (δ, ppm): 2.43 (7-CH$_3$), 3.23 (NCH$_3$), 6.31 (6-CH), 2.75 (4-CH$_2$), 3.57 (2-CH$_2$), and 2.04 (3-CH$_2$) (CF$_3$COOH).

1,6-Dimethyl-4-oxo-2,3,4,7-tetrahydropyrrolo[2,3-b]pyridine (XIII). A 4.6-g sample of VII was heated in the presence of catalytic amounts of p-toluenesulfonic acid at 200° for 1 h with removal of the alcohol by distillation. The mixture was then triturated with anhydrous ether and filtered. PMR spectrum (δ, ppm): 2.24 (6-CH$_3$), 2.91 (NCH$_3$), 5.81 (5-CH), 2.82 (3-CH$_2$), and 3.52 (2-CH$_2$) (CD$_3$OD).

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STEREOCHEMISTRY OF 2,7-DISUBSTITUTED

AND 1,2,7-TRISUBSTITUTED

4-ALKYLDECAHYDRO-4-QUINOLOLS

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The configurations of the 2 and 4 centers in 1,2,7-trimethyl-, 2,7-dimethyl-, and 1,2-dimethyl-7-tert-butyl-4-alkyldecahydro-4-quinolols were assigned on the basis of a comparison of the ^{I}[M-CH$_3$]$^+$/^{I}[M]$^+$ and ^{I}[M]$^+$ peak intensity ratios (the [M − CH$_3$]$^+$ and [M − C$_2$H$_5$]$^+$ ions are due to elimination of 2-CH$_3$ and 4-C$_2$H$_5$ groups, respectively) in the mass spectra of the stereoisomers.

A mass spectrometric method was previously used [1,2] for the determination of the configurations of the 2 and 4 centers in molecules of 1,2-disubstituted 4-alkyldecahydro-4-quinolols with trans fusion of the rings. In the present paper we present mass spectrometric data that make it possible to assign the configurations of the same centers in more complex 1,2,7-trisubstituted Ia-c, IIa-c, Va,c, and VIa,c and 2,7-disubstituted 4-alkyldecahydro-4-quinolols IIIa and IVa. The synthesis of the compounds under consideration will be

TABLE 1. Intensity Ratios of the Characteristic Peaks in the Mass Spectra of I-VI

Compound	mp, °C	$I_{[M-CH_3]^-}/I_{[M]^-}$	$I_{[M-C_2H_5]^-}/I_{[M]^-}$
Ia	126—127	8,2	—
IIa	118—119	5,7	—
Ib	98—99	7,4	—
IIb	89—90	4,4	—
Ic	113—114	7,0	2,5
IIc	99—100	5,5	3,0
IIIa	140,5—141	2,9	—
IVa	142—143	1,8	—
Va	102—103	7,3	—
VIa	99—100	3,4	—
Vc	118,5—119	7,9	3,1
VIc	114—115	4,6	2,3

described in a separate communication, but it is worth noting that with respect to the preparative method all of them have trans-fused rings. The affiliation of the ethynyl,. vinyl, and ethyl derivatives of I, II, V, and VI with steric series was proved by their interconversions during stepwise hydrogenation. The ethynyl derivatives (IIIa and IVa) of 2,7-dimethyldecahydro-4-quinolol have the same stereochemistry as the analogous derivatives (Ia and IIa, respectively) in the 1,2,7-trimethyldecahydro-4-quinolol series, inasmuch as they are converted to the latter on methylation. Insofar as the configuration of the 7 center in the investigated compounds is concerned, it cannot be assigned on the basis of the mass spectra, since specific fragments due to the presence of a 7-alkyl group are not observed in the spectra. However, considering the high conformational energy of the tert-butyl group, it can be assumed that it is equatorially oriented in V and VI.

I, III, V a-c   II, IV VI a-c
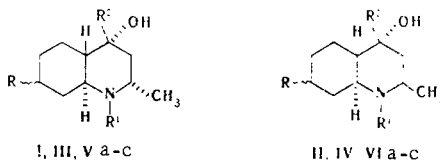
I, II R=R¹=CH₃; III, IV R=CH₃, R¹=H; V, VI R=tert-C₄H₉, R¹=CH₃; I—VI a R²= =C≡CH; b R²=CH=CH₂; c R²=C₂H₅

The mass spectra of all of the investigated compounds contain a small number of intense peaks. The maximum peak is that of the $[M - CH_3]^+$ ion, which corresponds to ejection of a CH_3 radical from the 2 position. In the case of 4-ethyl derivatives Ic, IIc, Vc, and VIc the $[M - C_2H_5]^+$ ions, which are due to ejection of a 4-C_2H_5 group, also have intense peaks. The peaks of the M^+ and $[M - C_3H_6R]^+$ ions (detachment of a portion of the carbocyclic ring with the substituent attached to C-7) have lower intensities. It should be noted that all of the principal fragments in the mass spectra under consideration are formed from the molecular ions, after which they undergo practically no fragmentation. In this situation one can use the kinetic approach to the mass spectra developed by Bursey and McLafferty [3] and consider the ratios of the intensities of the fragment and molecular ions to be the rate constants of the corresponding monomolecular reaction: $Z_X = k_X = I_{[F]}^+/I_{[M]}^+$.

The stereochemistry of the examined compounds has a primary effect on the rate of elimination of the 2-CH_3 group from the molecular ions: in the I, III, and V series the $I_{[M-CH_3]}^+/I_{[M]}^+$ intensity ratios are higher than the values for the corresponding epimers in the II, IV, and VI series. This difference in the rate of detachment of the 2-CH_3 group can be associated with the difference in the free energy of the epimers due to the axial or equatorial character of the 2-CH_3 group. In fact, when the 2-CH_3 group is axially oriented, there are 1,3-cis-diaxial interactions of this group with the axial substituent in the 4 position and the proton attached to C-9, and this increases the free energy of the compound and, as a consequence, the rate of detachment of the 2-CH_3 group as compared with the equatorial epimer, in which this interaction is absent. We have verified this principle in a number of other derivatives [1, 2]. Thus, considering the difference in the $I_{[M-CH_3]}^+$ peak intensity ratios, one can conclude that compounds of the I, III, and V group have an axial 2-CH_3 group, whereas alcohols II, IV, and VI have an equatorial 2-CH_3 group.

As we have already noted previously [1, 2], the configuration of the 4 center in 4-alkyldecahydro-4-quinolols affects the ratio of the intensities of the peaks of the $[M - alkyl]^+$ and M^+ ions, and this value is higher in the case of an axial orientation of the 4-alkyl group than in the case of an equatorial orientation [this comparison is possible only for compounds with saturated alkyl groups (for example, ethyl), inasmuch as the ethynyl and vinyl groups are not detached under electron impact]. In the case of the compounds examined in the present research, we did not have epimers at the 4 center, and this makes it impossible to make this sort of quantitative comparison. However, the $I_{[M-C_2H_5]}^+/I_{[M]}^+$ ratios in the spectra of Ic, IIc, Vc, and VIc make it possible

to conclude with a high degree of probability that all of the compounds considered have a 4e-alkyl-4a-OH configuration. In fact, as we have previously shown [1, 2], regardless of the length of the alkyl substituent in the 4 position (C_2H_5 or n-C_4H_9), this ratio for the axial group lies within the limits of eight and is close to four for an equatorial group. The $I_{[M-C_2H_5]}$ +/$I_{[M]}$ + ratios in the spectra of the alcohols (Ic, IIc, Vc, and VIc) are less than four, and this may constitute evidence for an equatorial orientation of the 4-alkyl group in all I-VI.

EXPERIMENTAL

The mass spectra were obtained with a commercial MKh-1303 spectrometer with direct introduction of the sample into the ion source at 40°; the ionization energy was 70 eV, and the ionization chamber temperature was 150°. The reproducibility of the mass spectra was verified by repeated recording on different days; the error in the measurement of the peak ratio did not exceed 5 rel. %.

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IONIZATION POTENTIALS OF DIPYRIDYLS
AND DIQUINOLYLS

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The ionization potentials of a number of isomeric dipyridyls and diquinolyls were determined. The differences in their values make it possible to establish the site of fusion of the rings in the 2,2', 3,3', and 4,4' positions of the system. The absence of an appearance potential for the fragment ion, the existence of which is due to cleavage of the interannular bond in the doubled hetaryl compounds, constitutes evidence for its double-bond character.

According to the concepts of Szent-Györgyi [1], the physiological activity of many organic substances is due to their donor properties, which are manifested in an increased tendency to form charge-transfer complexes (CTC). In this connection, research to determine the ionization potentials (IP) of various dipyridyls and diquinolyls, the diverse physiological activities of which have been studied, seems to us extremely useful, inasmuch as the accumulation of such data opens up prospects for the prediction of the biological action of new substances from their IP. The present research may also be of interest for the evaluation of the correctness of quantum-chemical calculations of bisheteroaromatic systems, since the IP correspond at least approximately to the energy of the higher occupied molecular orbital (the Copman theorem) [2].

In a previous mass spectrometric study of dipyridyls [3] and diquinolyls [4], we were unable to unambiguously establish whether the bond between the hetaryl rings in their molecules is cleaved or whether the peaks of ions with masses equal to the mass of one ring of the system are represented exclusively by doubly charged ions.

In the present study we made an attempt to use the IP of the corresponding fragment ions for this purpose. The IP for a number of isomeric dipyridyls and diquinolyls are presented in Table 1.