The ratio of III and IV in the crude mixture, which was similarly determined from the signals at 2.54 ppm for III and at 6.47 for IV, was 8.4:1.

3-Carbethoxy-2,5-dimethyl-5-(3-buten-1-ynyl)- and 3-Carbethoxy-2-methyl-5-(3-methyl-3-buten-1-ynyl)-4,5-dihydrofurans (V, VI). Similarly, the reaction of 1.5 g (7 mmole) of $Cu(OAc)_2 \cdot 2H_2O$ in 65 ml of acetic acid, 26.8 g (0.1 mole) of $Mn(OAc)_3 \cdot 2H_2O$, 26.0 g (0.2 mole) of acetoacetic ester, and 9.2 g (0.1 mole) of vinylisopropenylacetylene gave 30.1 g of a crude product containing, according to GLC data, V and VI in a ratio of 9:1. The crude mixture was distilled, and the fraction with bp 90-140°C (1.3 hPa) was collected. Redistillation gave 7.0 g (64%) of V with a purity of 94%.

IR spectrum for V: 3110 (=C-H); 2225 (C≡C); 1698, 1685 (splitting of $COOCH_2CH_3$); 1645 (dihydrofuran ring C=C); 1610 cm^{-1} (C=C). UV spectrum, λ_{max} (log ε): 215 (3.90), 223 (3.97), 232 (3.95), and 258 nm (3.98). PMR spectrum: 1.24 (3H, t, $3-COOCH_2CH_3$), 1.61 (3H, s, $5-CH_3$), 2.16 (3H, t, $2-CH_3$), 3.00 (2H, center of an ABX_3 system, CH_AH_B), 4.12 (2H, q, $3-COOCH_2CH_3$), and 5.30-5.88 ppm (3H, vinyl group), $J_{H_A-H_B} = 13.9$, $J_{CH_3-CH_2} = 7.0$, $J_{2-CH_3-H_{A(B)}} = 1.6$ Hz.

Compound VI was identical with respect to the results of GLC (retention time 15.8 min under the conditions of the GLC experiment presented in Table 1 for V) to a genuine sample obtained by a similar reaction form dimethylvinylethynylcarbinol.

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MASS SPECTRA OF cis- AND trans-4-ALKYL-3-PHENYL-3,4-DIHYDROCOUMARINS

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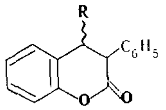
An analysis of the mass-spectrometric behavior of cis- and trans-4-alkyl-3-phenyl-3,4-dihydrocoumarins makes it possible to distinguish each of the isomers when the mass spectra of the two compounds are simultaneously present.

We have previously developed a method for the synthesis of isomeric cis- and trans-4-alkyl-3-phenyl-3,4-dihydrocoumarins [1], and we have recently determined the geometry of each of them by PMR spectroscopy [2, 3]. It seemed of interest to attempt to find the mass-spectrometric characteristics of this group of compounds, which would make it possible to identify similar geometrical isomers. For this, we studied the behavior of a series of cis and trans isomers of 4-alkyl-3-phenyl-3,4-dihydrocoumarins (Ia, b-IVa, b) under electron impact.



Ia,b-IVa,b

a = cis, b = trans
I $R=C_2H_5$; II $R=CH(CH_3)_2$;
III $R=C(CH_3)_3$; IV $R=CH_2C_6H_5$

An analysis of the mass spectra obtained (see Table 1) shows that the molecular ions of the investigated compounds undergo fragmentation primarily via two pathways (see Scheme 1). They either lose a substituent in the 4 position with subsequent fragmentation of the resulting F_1 fragment to give F_2 and F_3 ions, which are characteristic for the fragmentation of cou-

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TABLE 1. Mass Spectra* of I–IV

Compound	Configuration	m/z (relative intensity, %)
Ia	cis	252 (62), 224 (15), 223 (30), 195 (32), 167 (27), 165 (16), 133 (14), 118 (100), 91 (22), 90 (28), 89 (17)
Ib	trans	252 (88), 224 (19), 223 (32), 195 (37), 167 (27), 165 (18), 133 (15), 118 (100), 91 (18), 90 (19), 89 (13)
IIa	cis	266 (48), 224 (17), 223 (100), 195 (39), 179 (17), 167 (39), 165 (19), 148 (22), 118 (36), 91 (12), 90 (17)
IIb	trans	266 (65), 224 (20), 223 (100), 195 (37), 179 (35), 178 (16), 167 (36), 165 (20), 152 (11), 148 (24), 118 (22)
IIIa	cis	280 (2), 224 (100), 223 (22), 207 (16), 167 (15), 165 (14), 147 (54), 146 (15), 118 (18), 91 (35), 57 (52)
IIIb	trans	280 (8), 224 (100), 223 (19), 207 (17), 167 (14), 165 (16), 147 (46), 146 (16), 118 (10), 91 (25), 57 (63)
IVa	cis	314 (16), 223 (100), 222 (16), 195 (26), 179 (29), 167 (32), 165 (19), 152 (12), 118 (14), 91 (26), 78 (15)
IVb	trans	314 (17), 223 (100), 222 (18), 195 (20), 179 (38), 178 (15), 167 (26), 165 (18), 152 (11), 118 (5), 91 (23)

*The **molecular-ion** peak and the 10 most intense peaks of fragment ions are presented.

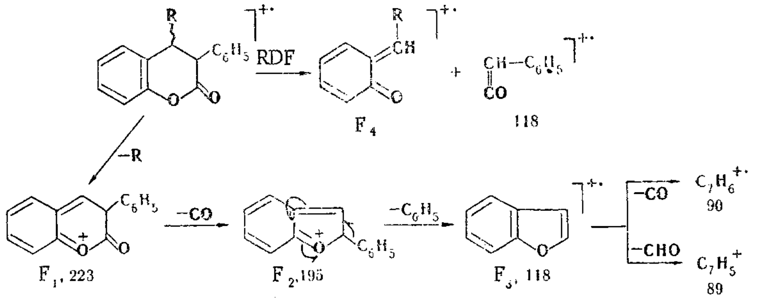
TABLE 2. Intensities of the Peaks of the Characteristic Ions (Σ_{39})

Compound	Configuration	W_M	F_1		F_2		F_3		F_4	
			I	I/I_M	I	I/I_M	I	I/I_M	I	I/I_M
Ia	cis	10,5	4,7	0,5	5,3	0,5	16,8	1,6	1,7	0,2
Ib	trans	12,3	4,4	0,4	5,3	0,4	14,2	1,1	1,3	0,1
IIa	cis	8,3	17,3	2,1	6,6	0,8	6,2	0,8	3,7	0,5
IIb	trans	10,9	16,7	1,5	6,4	0,6	3,8	0,3	4,2	0,4
IIIa	cis	0,3	17,4	50,7*	1,7	4,8	3,0	8,8	0,7	2,1
IIIb	trans	1,5	18,6	12,3*	1,4	0,9	1,9	1,3	—	—
IVa	cis	3,6	21,6	6,1	5,8	1,6	3,0	0,9	1,7	0,5
IVb	trans	4,1	23,6	5,8	5,1	1,2	1,1	0,3	1,1	0,3

*For the ion with m/z 224.

marins [4], or undergo retrodiene fragmentation **(RDF)** of the heterocyclic part of the molecule (F_4 ions and ions with m/z 118).* In the case of III the first process is also accompanied by transfer of one hydrogen atom from the departing alkyl group to the charged fragment. The resulting ion with m/z 224 subsequently loses successively a phenyl group and a CO molecule (Scheme 2).

Scheme 1



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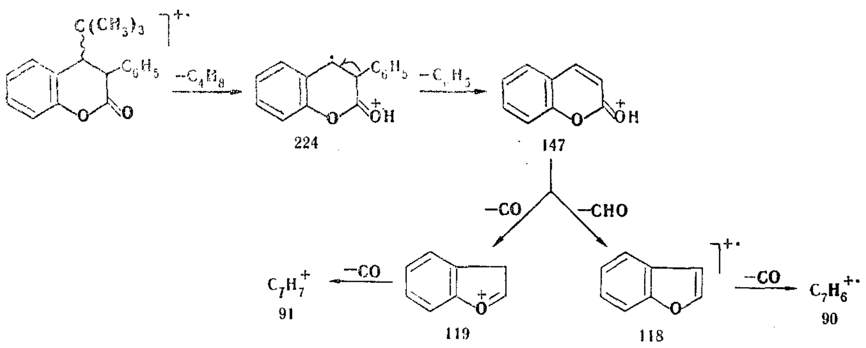
*The F_3 ion has the same m/z value as the F_4 ion (118). It is impossible to establish the fraction of each of the fragments in the overall current of the two ions. Here and subsequently in the text and in the schemes, the numbers that characterize the ions are the mass-to-charge ratios (m/z).

Scheme 2



Both fragmentation pathways indicated in Scheme 1 occur with involvement of the chiral centers of the molecule, and, as expected, the intensities of the peaks of the principal fragment ions and the stability of the molecular ion (W_M) are therefore associated with the geometry of the starting compound (see Table 2). As a rule, the W_M values are greater for the trans isomers, and the intensities of the peaks of the F_1–F_4 ions are higher for the cis isomers.

The mass-spectrometric differences between these two groups of compounds are even more appreciable when one compares the ratios of the intensities of the peaks of the fragment and molecular ions. This makes it possible to confidently determine the stereochemistry of each compound when both isomers are present. However, these differences are not great enough to make it possible to determine the configuration of the substituents in the 3 and 4 positions from the mass spectrum of only one isomer.

EXPERIMENTAL

The synthesis of the substances was described in [1]. The mass spectra were recorded with an LKB-2091 spectrometer with direct introduction of the samples into the ion source at an ionization energy of 70 eV.

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