in a dose of 1000 $TCID_{50}$ in a volume of 1 ml. The investigated preparations were titrated by dilution of the culture medium (with 5% hemhydrolyzate) to concentrations of 500, 50, and 5 μg/ml. Corresponding controls of the cytopathogenic activity of the virus, controls of the medium without the addition of the preparation, and controls of the toxicities of the investigated substances without the introduction of the virus were set up. The cytopathogenic activity of the virus in the controls and in the presence of the investigated preparations was evaluated 24, 48, 96, and 120 h after inoculation of the cell culture.

LITERATURE CITED

1. C. K. Chu and S. J. Cutler, J. Heterocycl. Chem., 23, 289 (1986).
2. A. E. Yavorskii, A. V. Stetsenko, S. G. Zavgorodnii, and V. L. Florent'ev, Khim. Geterotsikl. Soedin., No. 2, 198 (1988).
3. W. T. Smit and E. C. Stenly, J. Am. Chem. Soc., 75, 2192 (1953).
4. T. L. Tsilevich, S. G. Zavgorodnii, U. Marks, L. V. Ionova, and V. L. Florent'ev, Bioorg. Khim., 12, 819 (1986).
5. Organic Syntheses, Collective Vol. 4, Wiley, New York (1953).

MASS SPECTRA OF LIQUID CRYSTALS.

2.* ESTERS OF ALKOXY-SUBSTITUTED NICOTINIC AND PICOLINIC ACIDS

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Esters of alkoxypicolinic and alkoxynicotinic acids are reliably identified by means of their mass spectra and PMR spectra. While the alkoxypyridoyl cation in the case of the β esters undergoes fragmentation only with the successive splitting out of an olefin via the McLafferty mechanism and then a CO molecule, these processes also take place in the reverse order in the case of the α esters. The principal characteristic fragment ions by means of which such compounds in liquid-crystal mixtures can be identified and quantitatively determined were established.

In a previous study [1] we established the basic principles of the fragmentation of arylalkylpyridines under electron impact and determined the characteristic fragment ions, the signals of which can be used for the identification and qualitative and quantitative analysis of similar compounds in liquid-crystal compositions. The present communication is devoted to the mass-spectral investigation of aryl esters of alkoxy-substituted picolinic and nicotinic acids (I-IX), which are also liquid-crystal mesogens.

It is apparent from the PMR spectral data (Table 1) that the signals of the α, β, and γ protons of the pyridine ring are highly characteristic. The magnetic anisotropy of the carbonyl group in the case of the esters of nicotinic acid is responsible for deshielding of the γ protons, and their signal is shifted to weak field (~8.15 ppm). The signal of the β protons is shifted to weak field (~8.1 ppm) in the case of the esters of picolinic acid. These data make it possible to reliably distinguish the isomeric compounds.

The relative intensities of the peaks of the molecular and characteristic fragment ions are presented in Table 2. In some cases the M^+ peaks have insignificant intensities; this is due to facile cleavage of the ester bond, in which a substituted phenoxy radical is eliminated in the form of a neutral fragment, and the charge is always retained on the pyridoyl

*See [1] for Communication 1.

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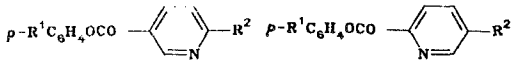
0009-3122/88/2405-0518$12.50

TABLE 1. PMR Spectra (in $CDCl_3$) and Mass Spectra of Esters I-XI



I–VII VIII, IX

Compound	R^1	R^2	Chemical shift, δ, ppm						m/z values (relative intensities of the ion peaks in percent of the maximum)[5]*
			H_α*	H_β**	H_γ	CH_2OPh***, CH_2Ph	CH_2OPy	C_6H_4[4]**	
I	$C_6H_{13}O$	OC_4H_9	8,88 d	6,71 d	8,12 dd	3,90 t	4,37 t	6,85 d; 7,02 d	371 (10), 179 (12), 178 (100), 140 (3), 123 (5), 122 (60), 110 (4), 94 (4), 43 (5), 41 (3)
II	$C_6H_{13}O$	OC_6H_{13}	8,92	6,72	8,18	3,93	4,35	6,85; 7,02	399 (10), 207 (20), 206 (100), 123 (8), 122 (96), 110 (7), 109 (4), 94 (5), 43 (10), 41 (4)
III	$C_6H_{13}O$	OC_8H_{17}	8,88	6,72	7,15	3,88	4,38	6,92; 7,12	428 (4), 427 (12), 235 (19), 234 (100), 123 (7), 122 (80), 110 (6), 94 (3), 43 (9), 41 (4)
IV	CH_3O	OC_8H_{17}	8,93	6,72	8,23	3,78	4,38	6,92, 7,13	357 (6), 235 (12), 234 (69), 124 (3), 123 (10), 122 (100), 95 (2), 94 (4), 43 (3), 41 (3)
V	C_6H_{13}	OC_8H_{17}	8,98	6,75	8,18	2,62	4,38	7,15 s	411 (4), 235 (19), 234 (98), 123 (8), 122 (100), 107 (5), 94 (5), 55 (3), 43 (6), 41 (3)
VI	C_6H_{13}	OC_6H_{13}	8,98	6,75	8,18	2,62	4,38	7,15 s	383 (3), 207 (19), 206 (100), 123 (8), 122 (84), 107 (8), 94 (6), 55 (3), 43 (6), 41 (3)
VII	NC—CH=CH	OC_5H_{11}	8,90	6,72	8,18	5,82[6]*	4,35	7,22—7,45 m; 5H ($4H_{Ar}H_{olef}$)	193 (10), 192 (82), 123 (7), 122 (100), 116 (2), 95 (2), 94 (9), 66 (3), 43 (4), 41 (3)
VIII	$C_6H_{13}O$	OC_4H_9	8,38	8,15	7,18	3,98	4,35	6,92; 7,05	371 (10), 179 (12), 178 (100), 150 (31), 122 (22), 110 (7), 109 (4), 94 (24), 43 (7), 41 (4)
IX	NC	OC_6H_{13}	8,35	8,02	7,15	—	4,35	7,32; 7,65	207 (15), 206 (100), 179 (6), 178 (19), 122 (37), 121 (6), 119 (11), 94 (33), 55 (6), 43 (10), 41 (7)
X	6-Methyl-3-pyridyl 4-(hexyloxy)benzoate		8,35	6,95	7,28	2,42	—	6,95; 8,12	206 (17), 205 (100), 122 (8), 121 (56), 120 (4), 93 (8), 92 (3), 65 (4), 43 (6), 41 (3)
XI	4-(2-Cyanovinyl)phenyl 4-(heptyloxyl)benzoate		—	—	—	3,92	5,55d; 6,95d[6]*	6,88; 7,15 7,38; 8,02	220 (18), 219 (100), 122 (9), 121 (92), 120 (6), 93 (8), 65 (4), 57 (4), 43 (4), 41 (4)

*$J_{\alpha\gamma}$ = 2 Hz.
**$J_{\beta\gamma}$ = 8 Hz.
***^3J = 6 Hz.
[4]**J_{AB} = 8.5 Hz.
[5]*The 10 most intense signals are presented.
[6]*Signals of the olefinic protons; J_{trans} = 16 Hz.

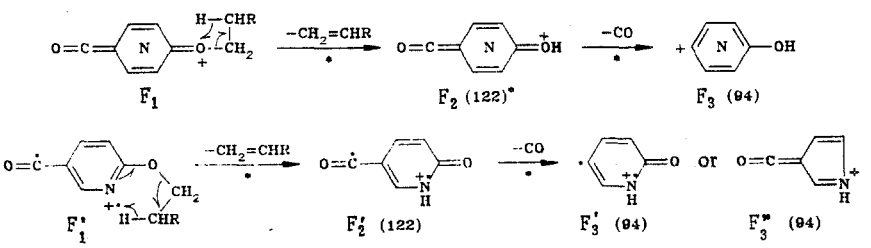
TABLE 2. Intensities of the Peaks of the Characteristic Fragment Ions in Percent of the Total Ion Current (Σ_{39})

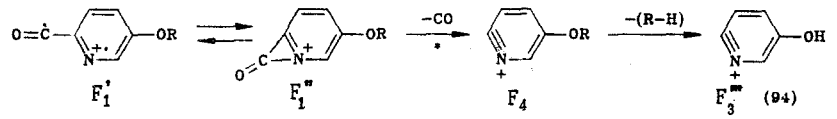
Compound	M^+	F_1	F_2	F_3	F_4	F_5	$\Sigma(M^+ + F_i)$
I	5,8	47,8	27,4	1,7	—	0,2	82,9
II	4,6	37,3	33,8	1,8	—	0,3	77,8
III	6,0	41,7	30,8	1,3	—	0,6	80,4
IV	3,6	34,8	46,5	2,0	—	0,8	87,7
V	1,8	40,3	37,9	1,9	—	0,8	82,7
VI	1,7	41,7	33,1	2,4	—	0,6	79,5
VII	0,4	37,1	43,2	3,9	—	0,2	84,8
VIII	5,0	42,9	9,0	9,6	13,2	—	79,7
IX	0,6	34,7	12,2	10,7	6,7	—	64,9
X	0,3	47,7	25,0	3,3	—	—	76,3
XI	<0,1	40,7	34,7	2,9	—	—	78,4

fragment (F_1), which has high-intensity (35-48%) signals. This is a unique fragmentation process that indirectly characterizes the substituents in the benzene ring of the investigated esters and, in any case, makes it possible to determine their masses. It is therefore important to note that the character of the substituents markedly affects the stabilities of the M^+ ions: for compounds that contain electron-donor alkoxy substituents (I-IV, VIII) W_M is 3.6-5.8, it decreases to 1.7 and 1.8 in the case of weak donors, viz., alkyl substituents (V and VI), and electron-acceptor substituents (VII and IX) decrease it to tenths. We recorded an M^+ signal in the spectra of all of the investigated compounds (sometimes with an increase in the voltage of the multiplier); however, one cannot exclude the possibility that M^+ ions cannot be recorded by the electron-impact method for other similar compounds and that information regarding the phenoxy part of the molecule cannot be obtained from the $m/z_{M^+} - m/z_{F_1}$ difference. For example, in the mass spectrum of liquid-crystal mesogen X, which is the carbocyclic analog of VII, an M^+ peak is virtually absent (at the noise level). In this case different but isomeric, in the pyridoyl part of the molecule (only with respect to the elementary composition and not with respect to the position of the alkoxy group in the pyridine ring; see below), compounds will give virtually the same mass spectrum and cannot be identified.

A common pathway of the fragmentation of pyridoyl cations F_1, which, in all likelihood, have a quinoid structure [2], is the successive splitting out of a molecule of an olefin (as a result of the migration of a hydrogen atom via a four-center mechanism [3]) and a CO molecule with the formation of F_2 and F_3 ions. Both of these processes are confirmed by corresponding metastable transitions. Attention should be directed to the fact that the relative intensities of the peaks of the F_2 ions in the spectra of the esters of nicotinic acids are significantly higher and the relative intensities of the peaks of the F_3 ions are significantly lower than in the spectra of the esters of picolinic acids (Table 2) and to the fact that in the case of the α esters the elimination also proceeds in the reverse direction, which is also confirmed by peaks of metastable ions. It might be assumed that the F_1 ions may also exist in the form of F_1' cation diradicals. Then an additional pathway of fragmentation of the F_1' diradicals with the formation of F_2' ions (the McLafferty rearrangement) appears in the case of the esters of nicotinic acids, while in the case of the esters of picolinic acids the F_1' cation diradical can form azirinone structure F_1'', which determines the elimination of a CO molecule.

The multipathway character of the processes involving the formation of the F_2 and F_3 ions and their different structures and stabilities determine the indicated differences in the relative intensities of the peaks of the common ions in the mass spectra of the isomers (I and VIII).

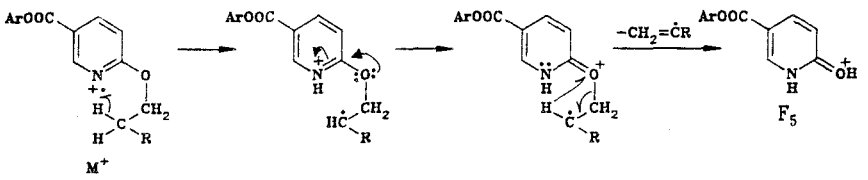




*The m/z values are presented in parentheses.

The formation of F_4 ions, the peaks of which have rather high intensities only in the mass spectra of the esters of picolinic acids, is a very important distinguishing mass-spectrometric feature that makes it possible to quantitatively determine the concentrations of the isomers when they are simultaneously present in mixtures by means of a chromatographic mass-fragmentographic method.

Another substantial difference in the fragmentation of the isomers is the fragmentation of the M^+ ions via a mechanism involving double rearrangement with splitting out of an alkenyl radical from the alkoxy group of the pyridine ring, which proceeds only in the case of the esters of nicotinic acids. Fragmentation with double migration of hydrogen atoms to the charged center in two successive processes and in one step was previously investigated [4, 5] primarily in the case of alkyl benzoates. As a rule, $[M - olefin]^+$ (single migration) and $[M - alkenyl]^+$ (double migration) fragments are formed simultaneously in this case. In the case of α-alkoxypyridines fragmentation only with double migration of hydrogen atoms has not been previously noted. It proceeds unambiguously and can be represented by the scheme [3]



It should be noted that a similar fragmentation process is not observed in the case of alkoxybenzoic acid ester XI.

The examined fragmentation of α-alkoxynicotinic acid esters is also an important distinguishing feature that makes it possible to distinguish regioisomers in the investigated series of compounds and also to determine the position of the alkoxy substituent in the pyridine ring.

EXPERIMENTAL

Compounds I-XI were previously synthesized [6]. The mass spectra were obtained with an MKh-1320 mass spectrometer; the ionizing voltage was 50 eV, the cathode emission current was 0.6 mA, and the temperature was 20-25°C (from the valve). The PMR spectra of solutions in $CDCl_3$ were recorded with a Tesla BS-467 spectrometer.

LITERATURE CITED

1. T. Yu. Samgina, P. A. Sharbatyan, L. S. Shishkanova, N. A. Andronova, A. I. Pavlyuchenko, and V. V. Titov, Khim. Geterotsikl. Soedin., No. 11, 1509 (1987).
2. P. B. Terent'ev, Mass Spectrometry in Organic Chemistry [in Russian], Vyssh. Shkola, Moscow (1979).
3. F. W. McLafferty, Interpretation of Mass Spectra, Univ. Sci. Books, Mill Valley, California (1982), p. 204.
4. D. V. Ramana and N. Sundarum, Org. Mass Spectrom., 16, 499 (1981).
5. C. Djerassi and C. Fenesalau, J. Am. Chem. Soc., 87, 5756 (1965).
6. A. I. Pavluchenko, N. I. Smirnova, E. I. Kovshev, and V. V. Titov, J. Phys. Collog., 40, 3 (1979).