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Simulation of Electron Ionization Mass Spectra of Cycloalkyl Fluorophosphonates

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Abstract—The mass spectra of highly toxic cycloalkyl alkylfluorophosphonates can be divided into two components: organophosphorus and hydrocarbon. The organophosphorus component is a generalized spectral image of a taxonomic group among those forming a homologous series of cycloalkyl alkylfluorophosphonates. The hydrocarbon component is interpreted as a spectrum of the cycloolefin which is the main product of cycloalkyl alkylfluorophosphonate fragmentation. A method for simulation of the electron ionization mass spectra of these compounds is proposed.

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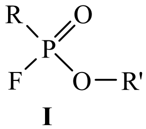
Alkyl alkylfluorophosphonates of the general formula **I** are highly toxic compounds which should be controlled under the Convention on the Prohibition of Chemical Weapons [1].



I

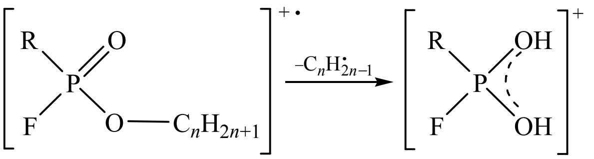
Here R is a non-cyclic alkyl radical containing 1 to 3 carbon atoms, R' is a non-cyclic or cyclic alkyl radical with 1 to 10 carbon atoms.

Developing the methods of identification of such compounds is obviously an important challenge. There are different approaches to the identification of organic compounds [2–4]. Among the most promising is the approach that forms the basis of the automatic expert systems or the artificial intelligence systems, as they were called formerly [2, 4, 5]. The identification process with such systems consists of several stages finalized by verification of the compliance of candidate structure and experimental spectra, using prediction of the spectra of possible structures. Currently, the methods of predicting spectra of the candidate structures created at one stage of the overall process became practically an independent branch of computer spectroscopy and mathematical chemistry [4]. This mainly concerns infrared spectroscopy and nuclear magnetic resonance [3, 4]. As for the mass spectra, as far as we know, the enough efficient general methodological approach to predicting mass spectra of not studied substances has not been developed [3, 6–8]. Meanwhile, gas chromatography–mass spectrometry is an important method for studying the toxic substances controlled under the Convention on the Prohibition of Chemical Weapons [1], especially in multicomponent mixtures [9], and therefore predicting the mass spectra of these substances is a very important issue.

Monitoring such substances is a rather complex task because some of their classes, in particular the major classes of organophosphorus toxic substances, contain dozens or even hundreds of thousands of individual substances [1]. At the same time, the professionals working in this field are in relatively good situation, because so far from 200 to 300 repressentatives of each major class of organophosphorus toxic substances have been studied that allows revealing quantitative and qualitative patterns of their decay under electron ionization. Based on these data, one can build the schemes for the simulation of mass spectra of unexplored compounds. We have proposed formerly the ways of modeling the mass spectra of alkyl alkylfluorophosphonates with non-cyclic alkoxyl radicals [10]. Note however, that the class of alkyl alkylfluorophosphonates is defined in the Convention

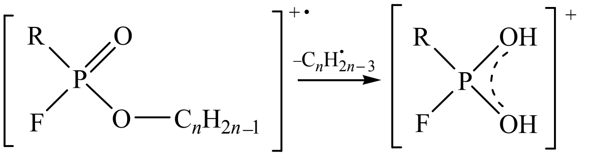
[1] as consisting of two homologous series. Most of the members of this class belongs to a series of cycloalkyl alkylfluorophosphonates. However, features of fragmentation of the compounds of this series, as we know, were never described, and the possibility of modeling their mass spectra was not investigated.

In [10] were noted two major directions of fragmentation of the alkyl alkylfluorophosphonate molecular ions with noncyclic alkoxyl groups. The first one is the cleavage of the olefin radical with the formation of the protonated alkylfluorophosphonic acid ion [Eq. (1)]. In the case of cycloalkyl alkylfluorophosphonates occurs respectively the cleavage of cycloolefin radical [Eq. (2)].



I **II**

(1)

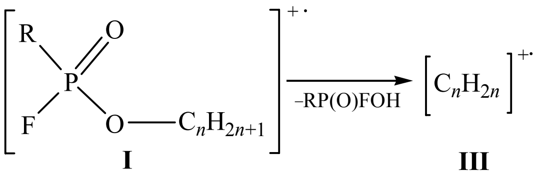


Ia **II**

(2)

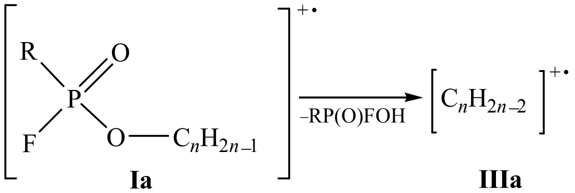
The second important direction is the rupture of the same bond between the ester oxygen atom and the first carbon atom of the alkoxyl radical followed by the migration of the hydrogen atom to the uncharged phosphorus-containing fragment [10]. This process results in the formation of olefinic molecular ion **III** [Eq. (3)].

In the case of decay of the cycloalkyl alkylfluorophosphonates, this process produces cycloolefinic molecular ion **IIIa** [Eq. (4)]. Reasonable to assume that in this case the same rules are fulfilled as in the case of alkyl alkylfluorophosphonates with non-cyclic alkoxyl radicals [10]: the carbon frame of alkoxyl radical exerts no changes in the process [Eq. (4)]; in the decay of the Eq. (4) type the hydrogen atom attached to the β-carbon atom of the alkoxyl radical, if available, is removed, and the double bond is formed in the nearest position to the ethereal oxygen atom, as shows Eq. (5).



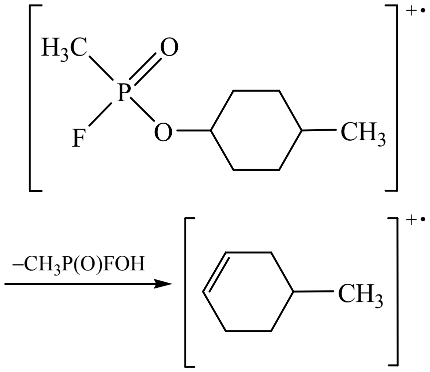
I **III**

(3)



Ia **IIIa**

(4)



(5)

Thus, while the structure and the mass of the ion **II** in the case of the alkyl alkylfluorophosphonates with non-cyclic and cyclic alkoxyl radicals are identical, in the case of the ion **III** there are significant differences: for the compounds of our interest the alkoxy group has cyclic structure, and at the same number of carbon atoms its mass number is by 2 Da less than in the case of acyclic analog. This leads to the main differences in the mass spectra of alkyl alkylfluorophosphonates with non-cyclic and cyclic alkoxyl radicals.

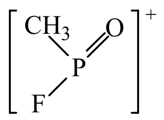
In [10] was indicated that the mass spectrum of an alkyl alkylfluorophosphonate can be represented as a sum (superposition) of organophosphorus and hydrocarbon components. The phosphorus component consists of a few peaks of the phosphorus-containing ions, while the hydrocarbon component is a mass spectrum of the olefin **III** (or, respectively, of cycloolefin **IIIa** in the case of cycloalkyl alkylfluorophosphonate). Noteworthy that the hydrocarbon component is individual for each compounds, while phosphorus component is a generalized spectral image of one of taxonomic groups forming a homologous series of cycloalkyl alkylfluorophosphonates. As the generalized spectral image [11, 12], we understand a subspectrum which is a permanent component of the spectra of all substances belonging to this taxonomic group. This subspectrum

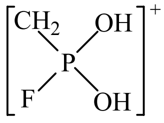
Table 1. Generalized spectral images (organophosphorus components of the mass spectrum) of taxonomic groups forming a homologous series of cycloalkyl alkylfluorophosphonates RP(O)F(OR)

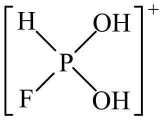
Group no.	R	Ion, *m/z* (I_{rel}, parts per thousand)
1	CH_3	**IV**, 81 (80); **II**, 99 (999)
1β	″	**IV**, 81 (80); **II**, 99 (999); **V**, 112 (200)
2	C_2H_5	**II**, 113 (999)
2β	″	**II**, 113 (999); **V**, 126 (200)
3	C_3H_7	**VI**, 98 (100); **II**, 127 (999)
3β	″	**VI**, 98 (100); **II**, 127 (999); **V**, 140 (50)
4	i-C_3H_7	**VII**, 85 (80); **II**, 127 (999)
4β	″	**VII**, 85 (80); **II**, 127 (999); **V**, 140 (50)

is characterized not only by the mass numbers of the peaks in it, but also by their relative intensity. In this work, as the taxonomic groups are considered the large groups of homologous series of cycloalkyl alkylfluorophosphonates differ by a radical at the phosphorus atom. In addition, in each of the large groups is distinguished a group of compounds with a branched β-carbon atom of the alkoxy radical: the mass spectra of such compounds differ signi-ficantly from those of other representatives of a large group. Thus, the homologous series of cycloalkyl alkylfluorophosphonates is divided into eight taxonomic groups. Their generalized spectral images are given in Table 1.

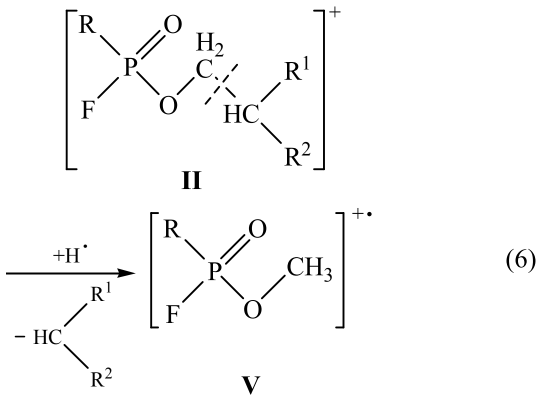
Structural formulas of the ions **IV, VI** and **VII** are listed below, the ways of their formation were described in [9, 10]. The peak intensities of these ions in the mass spectra of cycloalkyl alkylfluorophosphonates listed in Table 1 were estimated from the data for 24 compounds, where their peaks and the peaks of hydrocarbon ions produced by the decay of the olefin molecular ion **IIIa** are not superimposed.


IV


VI


VII

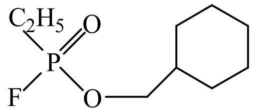
The ion **V** is formed in the reaction (6), which is a characteristic path of the decomposition of phosphoric esters [10].

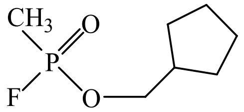

II

(6)

V

The degree of fragmentation by this way for alkyl alkylfluorophosphonates with acyclic alkoxyl radicals without branching at the β-carbon atom is very low, but increases by the order of magnitude and even more in the presence of such structural characteristics [10]. For cycloalkyl alkylfluorophosphonates observed the same pattern with the only feature that the compounds with the cyclic fragment attached to the first carbon atom of the alkoxy radical behave as the β-branched ones. Examples of such compounds are:





The procedure of constructing the electron ionization mass spectra of cycloalkyl alkylfluorophosphonates is very simple. To the mass spectrum of the model cycloolefin **IIIa** is added the peak of ion **II**. Its intensity is 200% of the maximum peak of hydrocarbon ion when the cyclic fragment contains less than three tertiary carbon atoms, and 150% when the number of such atoms is three or more. These figures are derived by generalization of the data for 40 cycloalkyl alkylfluorophosphonates. This dependence of intensity of the peak of the ion **II** on the structure of cycloalkoxyl radical is explained by the fact that upon increase in the branching the degree of fragmentation by path (2) increases in accordance with the well-known Stevenson–Odier rule [13]. Then to the simulated spectrum are introduced all the other peaks of phosphorus-containing ions of the given taxonomic group, with the intensities as listed in Table 1. If the mass numbers of peaks of hydrocarbon ions and the peaks of the input of phosphorus ions coincide, the intensity increases.

Example 1. Simulation of the mass spectrum of 4-ethylcyclohexyl methylfluorophosphonate. As an initial cycloolefin is taken 4-ethylcyclohexene. The spectrum of this compound is shown in Fig. 1a. The maximum hydrocarbon peak in this case is the peak at *m*/*z* 81. In accordance with the method described above, to the spectrum is added the peak at *m*/*z* 99 with 200% intensity relatively to the peak at *m*/*z* 81. Since in this case occurs imposition of the peaks at *m*/*z* 81 of 4-ethylcyclohexene and organophosphorus ion **IV**, the overall intensity of this peak is 50% + 8% = 58% (580 parts per thousand).

The simulated spectrum is shown in Fig. 1b, where it is compared in the head-to-tail manner with the experimental spectrum of 4-ethylcyclohexyl methylfluorophosphonate.

To check the quality of the simulated spectrum, it was processed with the information retrieval program NIST [14] for identification. Results of identification: the information retrieval program NIST showed first the correct structure. Indicators: Match (match for direct search) 873, R.Match (match by reverse search) 875. Since the maximum value of the indicators Match and R.Match is 1000, the correspondence can be considered as a very good.

Example 2. Simulation of the mass spectrum of cyclohexylmethyl ethylfluorophosphonate. The compound belongs to a taxonomic group 2β (Table 1). As an initial cycloolefin is taken methylencyclohexane, its spectrum is shown in Fig. 2a. The simulated spectrum is shown in Fig. 2b, where it is compared in a head-to-tail manner with the experimental spectrum of cyclohexylmethyl ethylfluorophosphonate.

Results of identification: the information retrieval program NIST puts the correct structure on the first place. Indicators: Match 844, R.Match 850. Thus, the

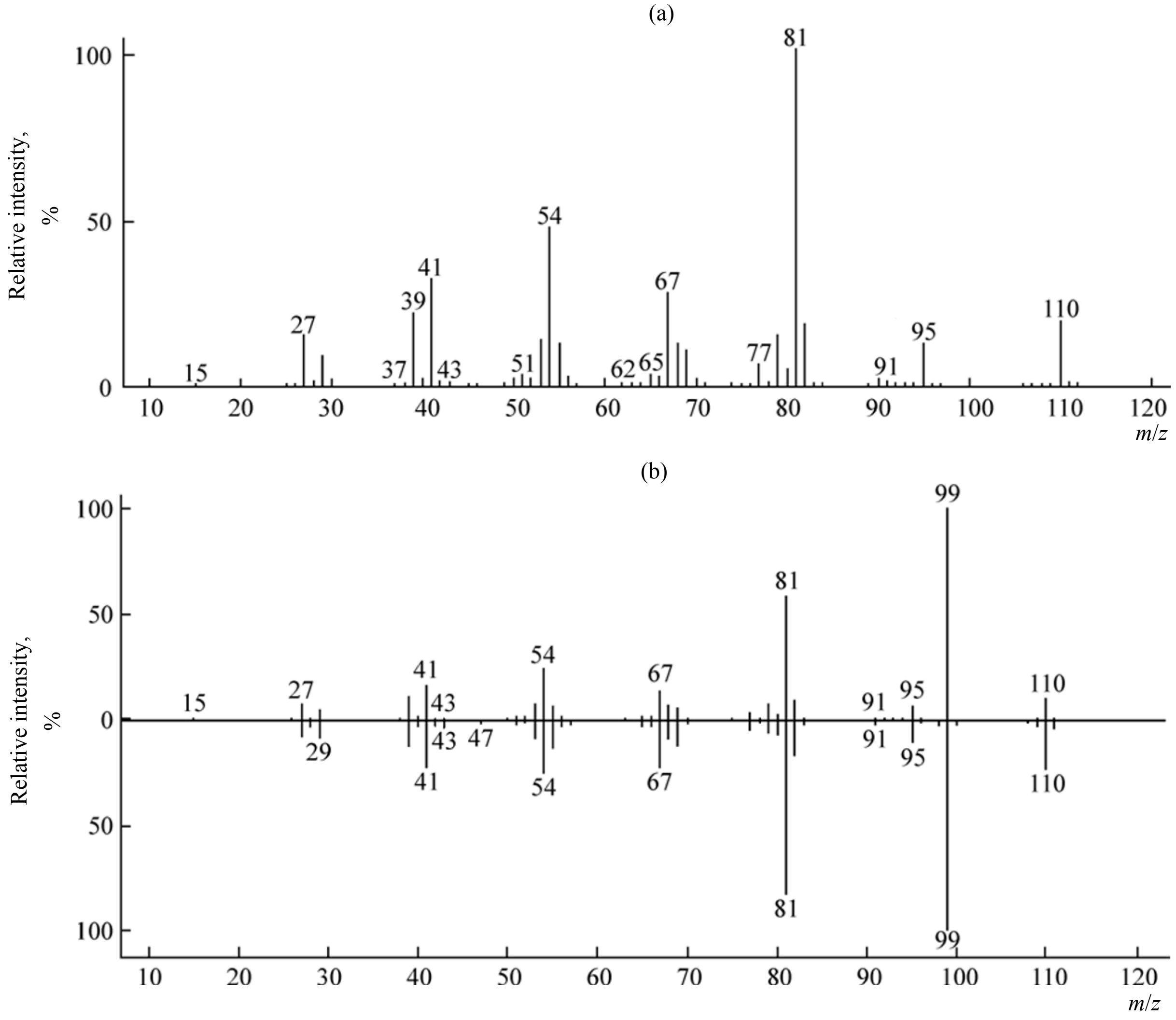


Fig. 1. (a) Spectrum of the initial 4-ethylcyclohexene and (b) Comparison of predicted (up) and experimental (down from the line of the mass numbers) spectra of 4-ethylcyclohexyl methylfluorophosponoates.

agreement between the experimental and the simulated spectrum can again be regarded as a very good.

Tables 2 and 3 show the simulation results of the mass spectra of cycloalkyl methyl- and ethylfluorophosphonates. In these tables, Match, R.Match, and Prob are the coincidence indices for forward and reverse search and the probability of correct structure, respectively, calculated with information retrieval program NIST [14].

From Tables 2 and 3 folows that the correct structures in most cases take first to third places in the list of the computer response, and rarely the fourth or fifth of a few tens of thousands of compounds contained in the databases of the NIST and OPCW libraries [15]. The values of Match, and R.Match vary in the range 690–890, which suggests a good agreement between experimental and predicted spectra. The reason for shift the right structure in rare cases to 4–5 place is the fact that the mass spectra of the isomers with the same carbon frame of the cycloalkoxyl radical are very similar, so that come into play the random factors of all sorts.

The results obtained for 20 cycloalkyl propyl- and isopropylfluorophosphonates are similar to those presented in Tables 2 and 3 for the methyl and ethyl homologues. The indicators Match and R.Match vary in the range 700–860, the correct structure in the list of answer takes from 1st to 7th place.

Thus, when the database of mass spectra includes corresponding cycloalkenes, the simulation of mass

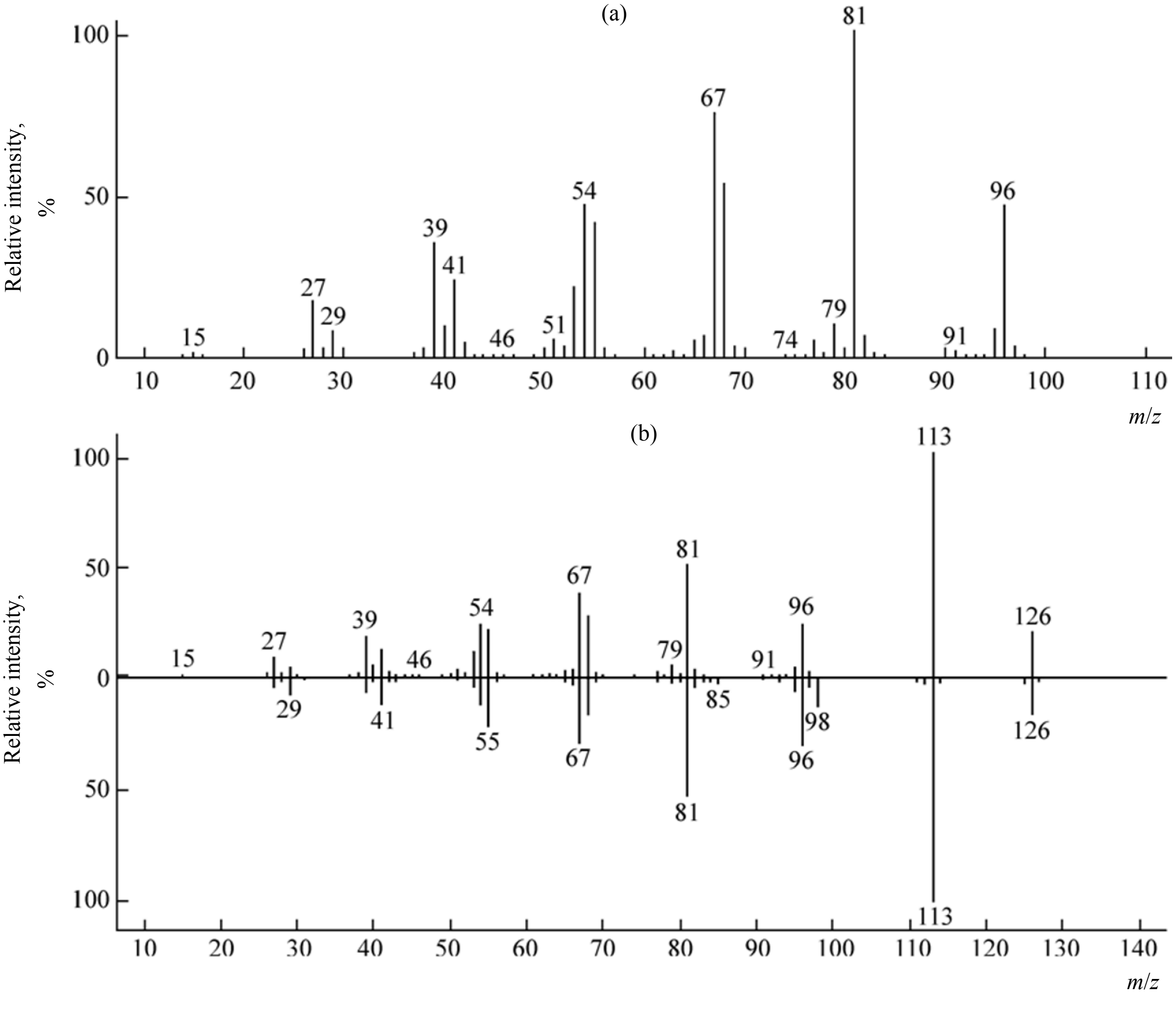


Fig. 2. (a) Spectrum of the initial methylenecyclohexane and (b) Comparison of predicted (up) and experimental (down from the line of the mass numbers) spectra of cyclohexylmethyl ethylfluorophosponates.

Table 2. The results of identification by search engine NIST MS SEARCH v.2.0 [14] of the predicted mass spectra of cycloalkyl methylfluorophosphonates $CH_3P(O)(OR)F$

Initial cycloalkene	Data of correct structure				
	Match	R.Match	Prob	position in the list	name
Cyclopentene NIST#: 227659	715	715	26.1	1	Cyclopentyl methylfluorophosponate
Methylencyclopentane NIST#: 238669	865	865	27.2	1	Cyclopentylmethyl methylfluorophosphonate
Cyclohexene NIST#: 114431	835	838	39.3	1	Cyclohexyl methylfluorophosphonate
4-Methylcyclohexene NIST#: 227868	851	852	22.6	2	4-Methylcyclohexyl methylfluorophosphonate
1-Methylcyclohexene NIST#: 231491	858	890	18.3	3	2-Methylcyclohexyl methylfluorophosphonate
Cycloheptene NIST#: 231486	816	836	5.9	5	Cycloheptyl methylfluorophosphonate
Methylencyclohexane NIST#: 235403	859	864	17.0	1	Cyclohexylmethyl methylfluorophosphonate
4-Ethylcyclohexene NIST#: 142679	873	875	44.4	1	4-Ethylcyclohexyl methylfluorophosphonate
3,5-Dimethylcyclohexene NIST#: 113432	814	831	7.5	2	3,5-Dimethylcyclohexyl methylfluorophosphonate
Cyclooctene NIST#: 113472	861	870	17.0	1	Cyclooctyl methylfluorophosponate
3-Cyclopentyl-1-propene NIST#: 34650	734	734	12.0	3	3-Cyclopentylpropyl methylfluorophosphonate
3,3,5-Trimethylcyclohexene NIST#: 34526	866	891	44.3	1	3,3,5-Trimethylcyclohexyl methylfluorophosphonate
3-Cyclohexyl-1-propene NIST#: 235709	764	772	19.2	2	3-Cyclohexilpropyl methylfluorophosphonate
4-*tert*-Butylcyclo-1-hexene NIST#: 27670	864	866	61.4	1	4-*tert*-Butylcyclohexyl methylfluorophosphonate
3-Isopropyl-6-methylcyclohexene NIST#: 38905	878	881	39.9	1	2-Isopropyl-5-methylcyclohexyl methylfluorophosphonate
Ethylidencyclohexane NIST#: 118885	772	778	2.6	4	1-Cyclohexylethyl methylfluorophosphonate

spectra of cycloalkyl fluorophosphonates is a simple procedure that leads to good results. One limitation of this approach is the fact that, unlike the olefins, the databases contain a relatively small number of spectra of cycloolefins. Nevertheless, we estimate that the developed method allows to simulate the mass spectra of several hundreds of unexplored cycloalkyl alkylfluorophosphonates.

Table 3. The results of identification by search engine NIST MS SEARCH v.2.0 [14] of predicted mass spectra of cycloalkyl methylfluorophosphonates $CH_3P(O)(OR)F$

Initial cycloalkene	Data of correct structure				
	Match	R.Match	Prob	position in the list	name
Cyclopentene NIST#: 227659	687	687	19.4	1	Cyclopentyl ethylfluorophosponate
Methylencyclopentane NIST#: 238669	756	765	14.2	2	Cyclopentylmethyl ethylfluorophosphonate
Cyclohexene NIST#: 114431	817	817	61.9	1	Cyclohexyl ethylfluorophosphonate
4-Methylcyclohexene NIST#: 227868	822	825	31.5	3	4-Methylcyclohexyl ethylfluorophosphonate
1-Methylcyclohexene NIST#: 231491	895	896	24.2	1	2-Methylcyclohexyl ethylfluorophosphonate
Cycloheptene NIST#: 231486	758	754	0.9	4	Cycloheptyl ethylfluorophosphonate
Methylencyclohexane NIST#: 235403	844	850	17.2	1	Cyclohexylmethyl ethylfluorophosphonate
4-Ethylcyclohexene NIST#: 142679	811	823	18.0	3	4-Ethylcyclohexyl ethylfluorophosphonate
3,5-Dimethylcyclohexene NIST#: 113432	841	854	16.3	1	3,5-Dimethylcyclohexyl ethylfluorophosphonate
Cyclooctene NIST#: 113472	838	844	20.6	1	Cyclooctyl ethylfluorophosponate
3-Cyclopentyl-1-propene NIST#: 34650	758	767	27.6	2	3-Cyclopentylpropyl ethylfluorophosphonate
3,3,5-Trimethylcyclohexene NIST#: 34526	844	867	35.8	1	3,3,5-Trimethylcyclohexyl ethylfluorophosphonate
3-Cyclohexyl-1-propene NIST#: 235709	728	728	13.9	2	3-Cyclohexilpropyl ethylfluorophosphonate
4-*tert*-Butylcyclo-1-hexene NIST#: 27670	813	820	55.9	1	4-*tert*-Butylcyclohexyl ethylfluorophosphonate
3-Isopropyl-6-methylcyclohexene NIST#: 38905	870	874	71.0	1	2-Isopropyl-5-methylcyclohexyl ethylfluorophosphonate
Ethylidenecyclohexane NIST#: 118885	754	759	2.0	5	1-Cyclohexylethyl ethylfluorophosphonate

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