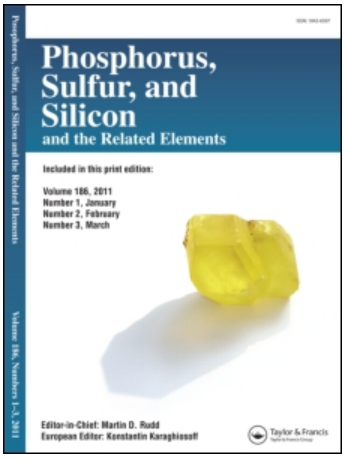

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Characterization of 1-Aminoalkanephosphonic Acids by Chemical Ionization Mass Spectrometry

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CHARACTERIZATION OF 1-AMINOALKANEPHOSPHONIC ACIDS BY CHEMICAL IONIZATION MASS SPECTROMETRY

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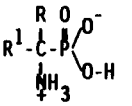
Chemical ionization mass spectra (CIMS and DCIMS) of 1-aminoalkanephosphonic acids **1** and their diester derivatives **3** are reported and they are discussed in the context of structural determination.

Key words: 1-aminoalkanephosphonic acids, chemical ionization mass spectra.

INTRODUCTION

Aminoalkanephosphonic acids **1**[1,2,4,6] belong to important class of phosphoroorganic compounds due to their structural analogy to natural amino acids[3,5] and also due to their chelating abilities.[1,2,6]



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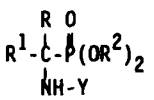
This importance involves also the research focusing on the direct analysis of aminoalkanephosphonic acids **1**. Considering the potentially useful methods of analysis of 1-aminoalkanephosphonic acids, the most prospective analytical capability seems at present the phosphorus nuclear magnetic resonance (the limitations are presented in the section results and discussion) and the mass spectrometry techniques.

However, the zwitterionic nature of aminoalkanephosphonic acids **1** involves some limitations in the application of mass spectrometric techniques. Thus, amino acids **1** are not amenable to electron-impact mass spectrometry (EIMS) and also GC/MS techniques. Therefore their mass spectrometric analysis have usually been preceded by the derivatization of amino acids **1** into volatile, usually diester type derivatives **3**.[7–12]

*Presented at the 3rd ECOPHOS Symposium, Dusseldorf, April 6–9, 1994.



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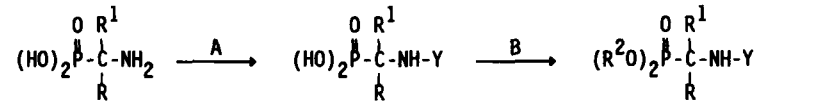
The alternative techniques for the structural analysis of 1-aminoalkanephosphonic acids **1** constitutes the fast atom bombardment mass spectrometry (FAB)[13,14] and the chemical ionization mass spectrometry (CIMS), using ammonia as a reagent gas.[15]

However, these pioneering works on the mass spectrometry of underivatized 1-aminoalkanephosphonic acids included only a few derivatives and these studies (especially CIMS) have not been continued.

In this paper we would like to present the results of our investigations on the chemical ionization (CIMS) and the direct chemical ionization mass spectrometry (DCIMS) of the underivatized 1-aminoalkanephosphonic acids **1**, using isobutane as a reagent gas.

The mass spectral study of the corresponding N-acylaminoalkanephosphonates **3**, obtained in the one-pot derivatization procedure from **1** (illustrated by Equation 1) are also discussed.



1	2	3
1a (R=R^1=H)	2B (Y=MeC(O))	3BA* (Y=MeC(O), R^2=Me)
1b (R=Me, R^1=H)	2C (Y=$CF_3C(O)$)	3BB* (Y=MeC(O), R^2=Et)
1c (R=Et, R^1=H)		3CA* (Y=$CF_3C(O)$, R^2=Me)
1d (R=Me, R^1=Me)		3CB* (Y=$CF_3C(O)$, R^2=Et)
1e (R=Bu, R^1=H)		3DA* (Y=$Me_3CC(O)$, R^2=Me)
1f (R=Ph, R^1=H)		3DB* (Y=$Me_3CC(O)$, R^2=Et)
1g (R=$PhCH_2$, R^1=H)		

A: Y-OH - Y-O-Y (Y = MeC(O), $CF_3C(O)$, $Me_3CC(O)$)

B: $R^3C(OR^2)_2$: (R^3= H, Me; R^2= Me, Et)

Taking into accounts the results of the presented investigations a possibility of application of the CIMS and/or GC/CIMS techniques for the analysis of a multicomponent mixtures of 1-aminoalkanephosphonic acids **1** is also presented.

EXPERIMENTAL

Materials. Acetic acid, acetic anhydride, trifluoracetic acid, trifluoroacetic anhydride, trimethylacetic acid, trimethylacetic anhydride, trimethyl orthoacetate, trimethyl orthoformate and triethyl orthoformate were purchased from Aldrich (Milwaukee, Ill., USA).

1-Aminoalkanephosphonic acids **1** have been prepared according to Reference 16. Other aminoalkanephosphonic acids and hydroxyalkanephosphonic acids were prepared according to Reference 17. All compounds investigated were of the purity as previously reported.

Gas Chromatography and Mass Spectrometry. A Finnigan MAT 95 mass spectrometer was used for GC/MS analysis of the multi component mixture of derivatives. Sample introduction was via the Varian

TABLE I

The conditions of the conversion of amino acids **1** into 1-(acylamino)alkanephosphonates **3**

3	R^1-C(O)-	R^2O-	Stage *A*		Stage *B*	
			Temp. (°C)	Time (h)	Temp. (°C)	Time (h)
3BA*	Me-C(O)-	MeO-	100	0.3	100	1.5
3BB*	Me-C(O)-	EtO-	100	0.3	100	1.5
3CA*	CF_3-C(O)-	MeO-	30-40	0.25	100	1.5
3CB*	CF_3-C(O)-	EtO-	30-40	0.25	100	1.5
3DA*	Me_3C-C(O)-	MeO-	100	2	100	2.5
3DB*	Me_3C-C(O)-	EtO-	100	2	100	2.5

3400 gas chromatograph equipped with a 30 × 0.25 mm I.D. capillary column BP-17. The column temperature was set to 100°C for 3 minutes and then with increased at a rate of 10°C min^{-1} to 250°C. The injector temperature was maintained at 200°C and the transfer line temperature was set to 250°C. The column was directly introduced to the ion source of the mass spectrometer. Mass spectra were recorded using isobutane as a reagent gas. The direct isobutane chemical ionization mass spectra (DCIMS) of the aminoalkanephosphonic acids and/or corresponding N-acylaminoalkanephosphonate **3** were also obtained on a Finnigan MAT 95 spectrometer. The samples were introduced in the ion source at 30°C and then the temperature increased to 360°C in 10 minutes and was kept at this level for 3 minutes.

Preparation of Derivatives **3**. The samples of 1-aminoalkanephosphonic acids **1** (0.1 to 5 mg) were dissolved in a carboxylic acid (0.05 ml) and its anhydride (0.05 ml) mixture and the resulting solutions were heated with stirring (st. *A*) under conditions indicated in Table I. Then the reaction mixtures were cooled to ca 40–50°C, and trialkyl orthoformate (0.4 ml) or trialkyl orthoacetate (0.4 ml) were added. The resulting mixtures were stirred at 100°C for the time indicated (st. *B*) and then were analyzed by GC/CIMS and/or CIMS techniques.

RESULTS AND DISCUSSION

The most spread out technique for the identification of phosphoroorganic compounds—^{31}P-NMR spectroscopy, is charged with some limitations when applied for the analysis of the functionalized alkanephosphonic acids (aminoalkanephosphonic acids bearing with the primary, secondary or tertiary amino group and/or hydroxyalkanephosphonic acids). These result from relatively small differences of the chemical shifts exhibited by several homologic phosphonic acids (Table II), and due to the strong and complex pH dependence of their chemical shifts,[18] at which the considered spectra are recorded. These properties for the most representative functionalized alkanephosphonic acids are presented in Table II.

TABLE II

The pH dependence of phosphorus chemical shift [d(P)] of functionalized alkanephosphonic acids (Proton decoupled spectra were recorded on a Bruker AC 200 spectrometer operating at 81.01 MHz)

Structure			^{31}P-M.R.J., δ (ppm)	
R^1	R^2	Y	1.9 N HCl	1.9 N KOH
H	H	NH_2	14.3	19.8
Me	H	NH_2	16.9	22.5
Et	H	NH_2	17.2	22.8
Me	Me	NH_2	19.6	25.6
Bu	H	NH_2	16.7	22.2
$PhCH_2$	H	NH_2	15.2	20.9
Ph	H	NH_2	12.9	18.6
H	$CH_2PO_3H_2$	NH_2	13.6, 14.3, 22.9, 23.6	22.07, 22.12
Et	H	NHMe	15.1	20.8
Ph	H	NHMe	11.4	16.5
Me	Me	NHEt	18.4	23.8
H	H	$NHCH_2CO_2H$	11.5	17.0
Me	H	NMe_2	13.3	19.9
Et	H	OH	24.7	18.6
Ph	H	OH	20.6	15.7
Me	Me	OH	27.6	21.5
Ph	Me	OH	15.6	10.4

Therefore is quite difficult on the basis of the ^{31}P-NMR spectrum of the mixture of aminoalkanephosphonic acids to determine their individual components. In addition, during an analysis can appear several factors (e.g. metal ions) which influence on a shape of the signals (broadening) and on this way increasing difficulty in its interpretation.

The mass spectral analysis of aminoalkanephosphonates is much more equivocal, especially when applying chemical ionization technique.

The Chemical Ionization of Underivatized 1-Aminoalkanephosphonic Acids **1**

The chemical ionization of 1-aminoalkanephosphonic acids **1a–g** were performed using isobutane as a reactant gas. The representative mass spectra (DCI and CI) of 1-aminopentanephosphonic acid (**1e**) are presented on Figures 1 and 2, respectively. The analysis of the evaporation curve revealed that amino acids **1** evaporate

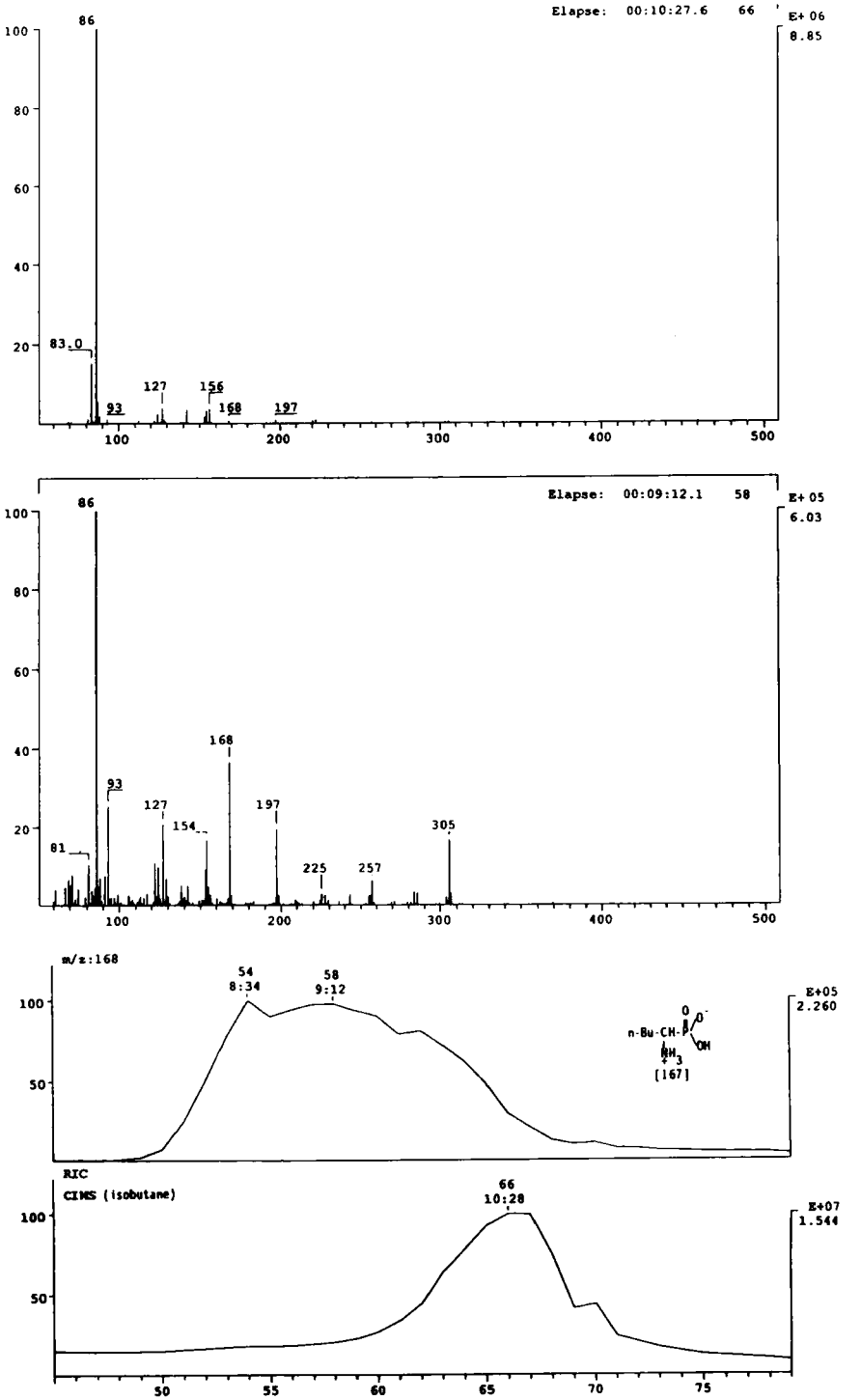


FIGURE 1 Isobutane chemical ionization mass spectra (CI) of the underivatized 1-aminopentanephosphonic acid **1e**.

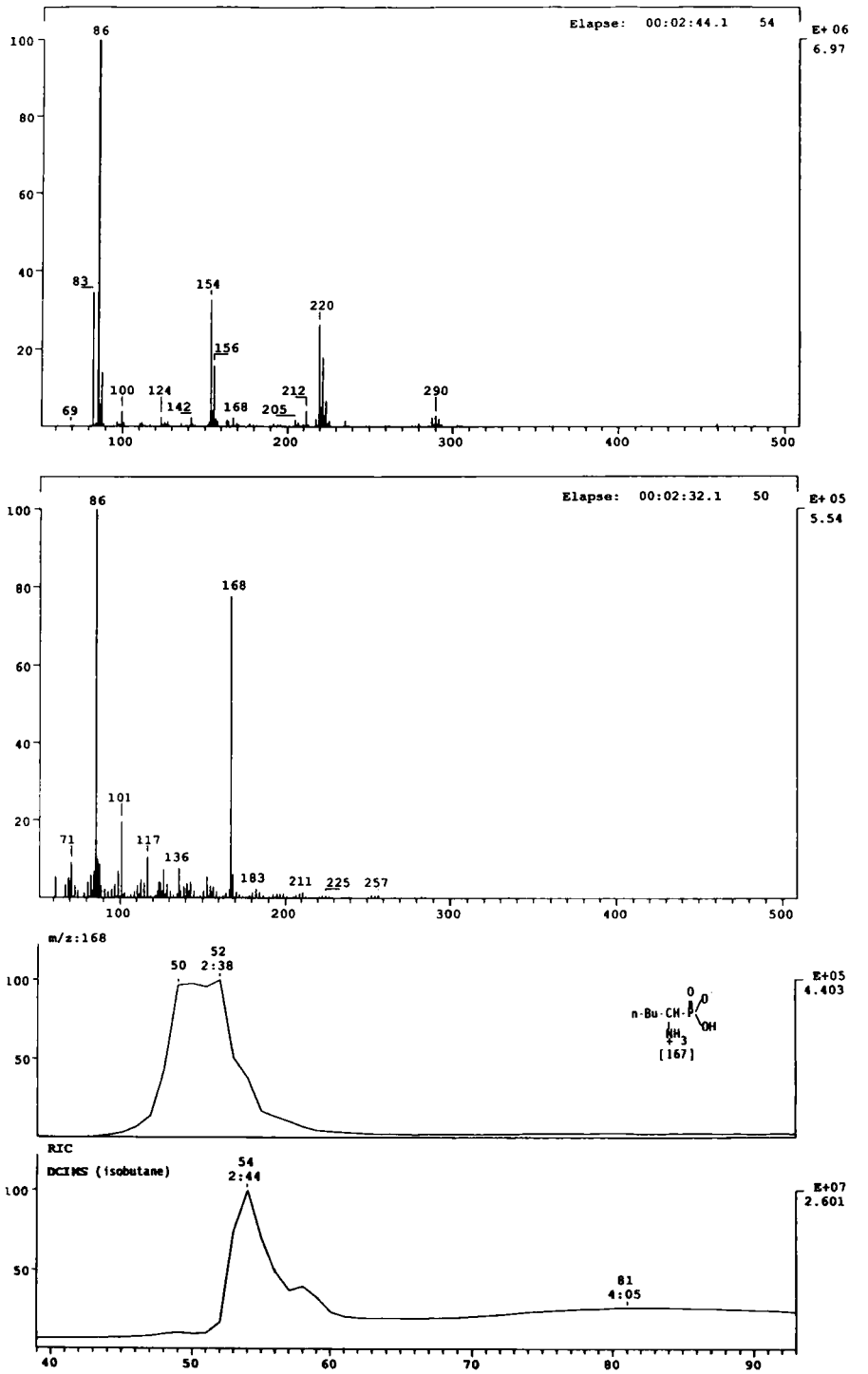


FIGURE 2 Isobutane direct chemical ionization mass spectra (DCI) of the underivatized 1-aminopentanephosphonic acid **1e**.

over 200°C (~10^{-4} Torr), at which they usually melt (or undergo decomposition) under atmospheric pressure.

The careful examination of these spectra reveals some contrast to the results obtained by Constantin and co-workers[13] under ammonia chemical ionization conditions.

These spectra (CIMS and/or DCIMS) also contain the protonated quasi molecular ions $[M + 1]^+$, however the contribution of their recombination ion current

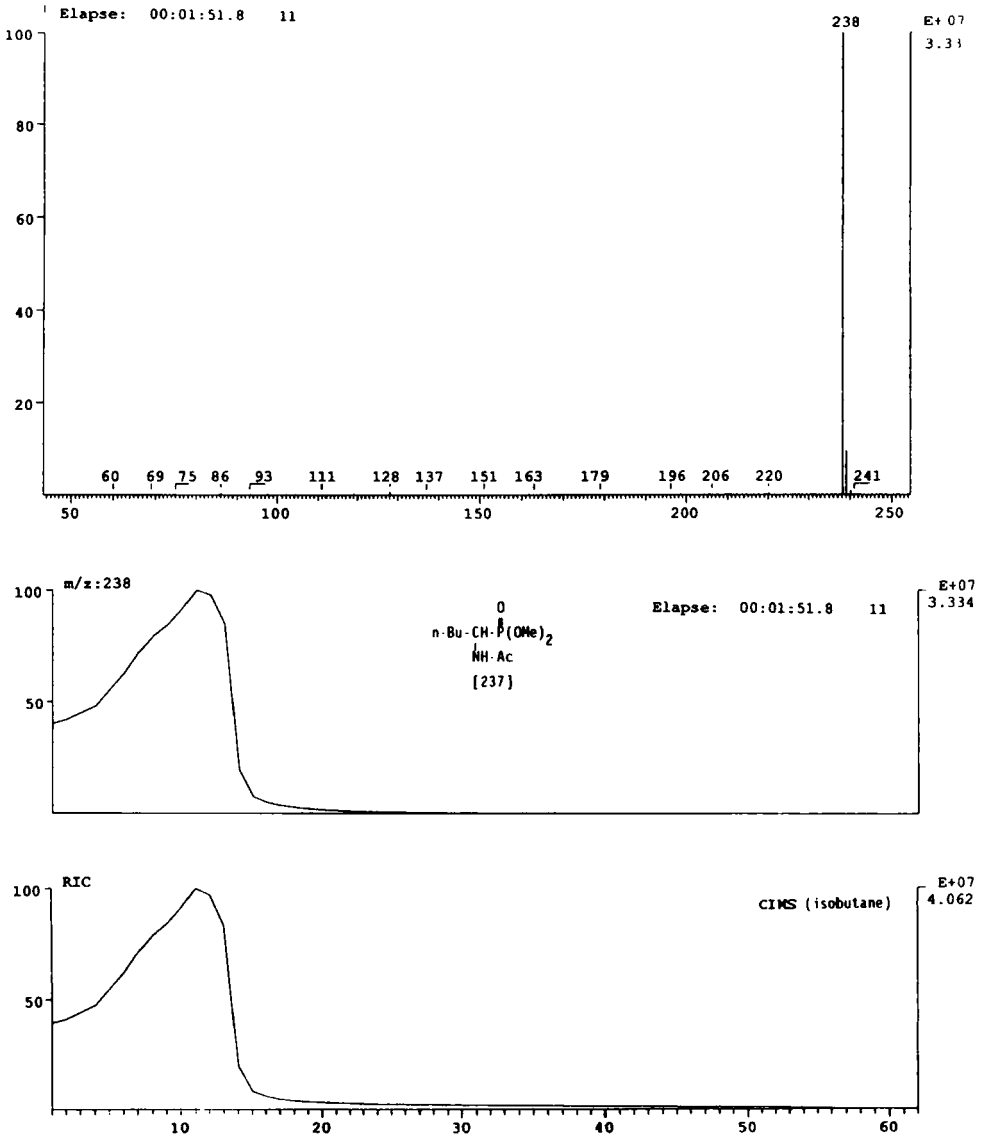


FIGURE 3 Isobutane chemical ionization mass spectra (CI) of the O,O-dimethyl 1-(N-acetylamino)pentanephosphonate **3BA*e** obtained by the derivatization of 1-aminopentanephosphonic acid **1e**, by means of the acetic anhydride-trimethyl orthoformate system, prior to the mass spectrometric analysis.

(RIC) consist only 1–2% of the total RIC (Figures 1 and 2). These [M + 1] ions appear at the beginning part of the evaporation curve occurring only in tracy amounts at the maximum of the total RIC.

Better, but still unsatisfactory results are obtained during the direct chemical ionization mode (DCIMS) of underivatized 1-aminoalkanephosphonic acids **1** (Figure 2). Thus, the evaporation of amino acids **1** occurs in this case faster than during CIMS mode (at lower temperatures), affording more coherent shape of the RIC and resulting less complexed mass spectra.

The base peaks of amino acids **1** in both techniques (CIMS and DCIMS) are correspond to the imine product, resulting from the elimination of phosphorous acid from the aminoalkanephosphonic molecule. Since an application of isobutane [M = 58] determines the lower limit of registration at m/z $\geq$ 60, these base peaks of **1** can be observed only in the mass spectra of higher aminoalkanephosphonic acids (e.g. **1e, 1f** and/or **1g**).

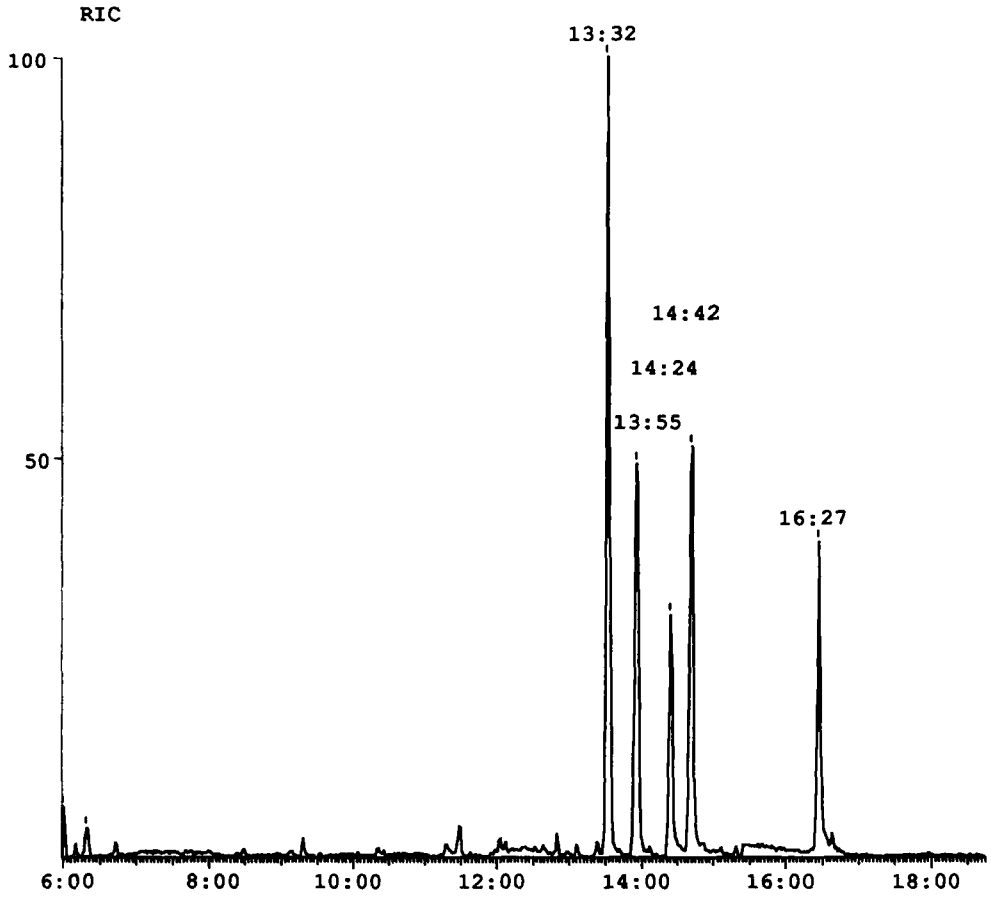


FIGURE 4 GC/CIMS chromatogram of the derivatization products of the mixture of 1-aminoalkanephosphonic acids **1a**, **1b**, **1c**, **1d** and **1e**, obtained by means of the acetic anhydride-trimethyl orthoformate system. Conditions are under experimental.

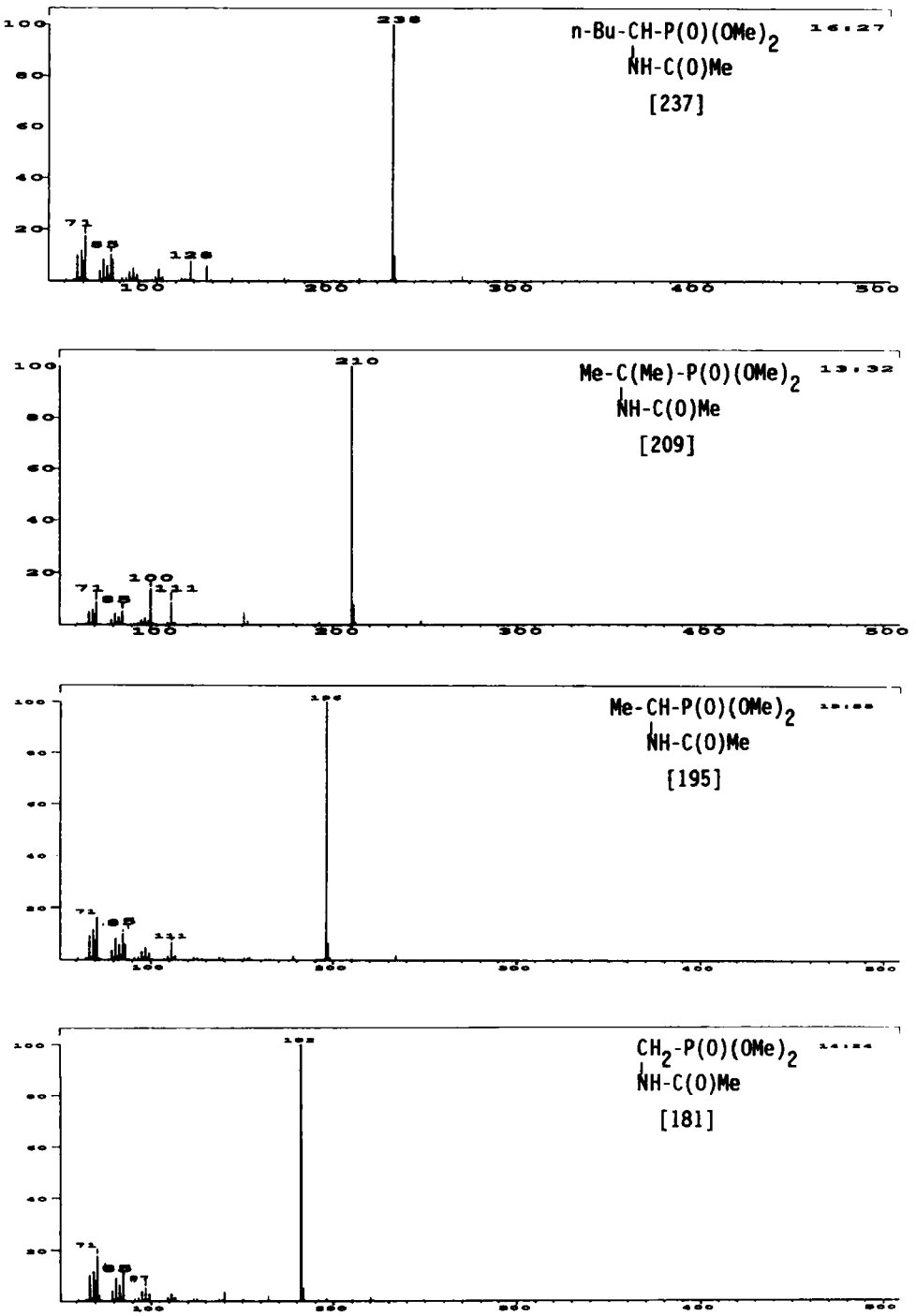


FIGURE 4A Isobutane chemical ionization mass spectra (GC/CIMS) of the mixture of O,O-dimethyl 1-(N-acetylamino)alkanephosphonates **3BA*** obtained by the derivatization of the mixture of 1-aminoalkanephosphonic acids **1a**, **1b**, **1c**, **1d** and **1e**, by means of the acetic anhydride-trimethyl orthoformate system, and separated chromatographically. Chromatogram is given in Figure 4.

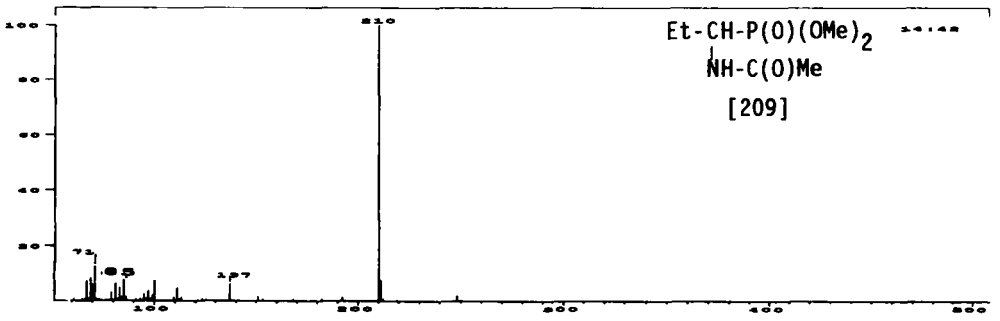


FIGURE 4A (*Continued*)

TABLE III

Reduced chemical ionization mass spectra of O,O-dimethyl 1-(acetylamino)alkanephosphonates **3BA***

No	R (R'= H)	Molecular formula (mass)	Mass spectrometry: m/z (relative intensity, %)				
			M+1	[M-41][a]	M - NHAc[b] [M-58]	M - P[c] [M-109]	P[d],j [111]
3BA•a	H	$C_5H_{12}NPO_4$	182	140[e]	123	72[j]	
		[181.1]	(100)	(3.7)	(1.0)		(4.9)
3BA•b	CH_3	$C_6H_{14}NPO_4$	196	154[f]	137	86[j]	
		[195.1]	(100)	(1.4)	(0.8)		(7.5)
3BA•c	C_2H_5	$C_7H_{16}NPO_4$	210	168[g]	151	100[j]	
		[209.2]	(100)	(0.6)	(1.7)	(8.0)	(7.2)
3BA•d	CH_3 (CH_3)	$C_7H_{16}NPO_4$	210	168[h]	151	100[j]	
		[209.2]	(100)	(0.2)	(4.6)	(10.2)	(9.0)
3BA•e	n-C_4H_9	$C_9H_{20}NPO_4$	238	196	179	128	
		[237.2]	(100)	(0.3)	(0.9)	(7.4)	(6.6)
3BA•f	C_6H_5	$C_{11}H_{18}NPO_4$	258	216	200	148	
		[257.2]	(100)	(0.3)	(2.0)	(11.0)	(9.0)
3BA•g	$C_6H_5CH_2$	$C_{12}H_{20}NPO_4$	272	230[i]	214	162	
		[271.2]	(100)	(-)	(0.2)	(4.0)	(10.0)

[a]M+1 - CH_2CO, [b]AcNH = $CH_3C(O)NH$-, M - P[c] = M - $(MeO)_2PO$, P[d] = $(MeO)_2P(H)OH$, [e]139 (0.5), [f]153 (0.8), [g]167 (0.3), [h]167 (0.4), [i]229 (0.3), [j]overlapping with the column background.

TABLE IV

Reduced chemical ionization mass spectra of O,O-diethyl 1-(acetylamino)alkanephosphonates **3BB***

No	R (R'= H)	Molecular formula (mass)	Mass spectrometry: M+1	[M-42][a]	M - NHAc[b] [M-58]	M - P[c] [M-137]	P[d] [139]
3BB•a	H	$C_7H_{16}NPO_4$	210	167[e]	151	72[h]	
		[209.2]	(100)	(3.5)	(3.9)		(3.5)
3BB•b	CH_3	$C_8H_{18}NPO_4$	224	181[f]	165	86[h]	
		[223.2]	(100)	(1.5)	(2.3)		(6.2)
3BB•c	C_2H_5	$C_9H_{20}NPO_4$	238	195	181	100	
		[237.1]	(100)	(0.2)	(2.0)	(6.0)	(6.5)
3BB•d	CH_3 (CH_3)	$C_9H_{20}NPO_4$	238	195	181	100	
		[237.1]	(100)	(0.3)	(2.1)	(9.5)	(7.9)
3BB•e	n-C_4H_9	$C_{11}H_{24}NPO_4$	266	223[g]	209	128	
		[265.3]	(100)	(0.2)	(1.9)	(9.0)	(8.0)

[a] [M+1 - $CH_3C(O)$] or [M - $CH_2C(O)$], [b] AcNH = $CH_3C(O)NH$-, M - P[c] = M - -$(EtO)_2P(O)$, P[d] = $(EtO)_2P(H)OH$, [e] 168 (2.8), [f] 182 (0.9), [g] 220 (1.2), [h] overlapping with the column background.

These fragments can arise from cleavage of the phosphorus-carbon bond, with proton transfer, to yield the ions $[M + H - H_3PO_3]^+$ (e.g. Equation 2), associated with the nitrogen-containing part of the molecule.

$$(HO)_2\overset{\beta}{P}(=O)\text{-}CH(\overset{\alpha}{\overset{\downarrow}{N}}H_3)\text{-}R \xrightarrow[\text{(eq. 2)}]{} (HO)_2\overset{\beta}{P}(=O)\text{-}H + H_2N{=}CH\text{-}R$$

However, due to a high temperature of evaporation of 1-aminoalkanephosphonic acids investigated, it is difficult to predict if these base peaks are formed as the products of chemical ionization of **1** (Equation 2), or formed from the corresponding imines—liberated from the parent aminoalkanephosphonic acids **1** during the pyrolisis. The analysis of the evaporation curves of **1** (e.g. **1e**, Figures 1 and 2) seems to support the latter assumption.

The remaining part of these mass spectra has only limited informative values. These facts suggest that an application of the chemical ionization mass spectrometric techniques for the structural analysis of underivatized 1-aminoalkanephosphonic

TABLE V

Reduced chemical ionization mass spectra of O,O-dimethyl 1-(trifluoroacetylamino)alkanephosphonates **3CA***

No	R (R'= H)	Molecular formula (mass)	Mass spectrometry:				
			M+1	M+1 - TFA[a] [M-96]	M - NHTFA[b] [M-112]	M - P[c] [M-109]	P[d,j] [111]
3CA*a	H	$C_5H_9F_3NPO_4$	236	139	123	126	
		[235.1]	(100)	(1.0)	(2.4)	(1.5)	(4.0)
3CA*b	CH_3	$C_6H_{11}F_3NPO_4$	250	153[e]	137	140	
		[249.1]	(100)	(0.4)	(2.0)	(3.0)	(10.6)
3CA*c	C_2H_5	$C_7H_{13}F_3NPO_4$	264	167[f]	151	154	
		[263.1]	(100)	(0.3)	(4.6)	(3.2)	(6.0)
3CA*d	CH_3 (CH_3)	$C_7H_{13}F_3NPO_4$	264	167[g]	151	154	
		[263.1]	(100)	(0.3)	(0.9)	(3.8)	(6.3)
3CA*e	n-C_4H_9	$C_9H_{17}F_3NPO_4$	292	195[h]	179	182	
		[291.2]	(100)	(<0.2)	(0.7)	(3.2)	(6.3)
3CA*f	C_6H_5	$C_{11}H_{15}F_3NPO_4$	312	215	199	202[i]	
		[311.2]	(100)	(0.7)	(1.3)	(7.6)	(9.5)
3CA*g	$C_6H_5CH_2$	$C_{12}H_{17}F_3NPO_4$	326	228	213	216	
		[325.2]	(100)	(0.2)	(0.9)	(3.8)	(13.0)

[a] TFA = $CF_3C(O)$-, TFANH = $CF_3C(O)$-NH-, M - P[c] = M - $(MeO)_2POH$, P[d] = $(MeO)_2P(H)OH$, [e] 151 (0.9), [f] 165 (0.7), [g] 165 (0.7), [h] 193 (0.6), [i] 201 (16.), [j] overlapping with the column background.

acids **1**, and also the analysis of their mixtures should be used with the prior derivatization of the parent amino acids **1** into more volatile compounds.

The Chemical Ionization of Derivatized-1-aminoalkanephosphonic Acids

Recently we have elaborated the two procedures for derivatization of 1-aminoalkanephosphonic acids **1** by means of orthoformate[11] and the anhydride-orthoester systems,[12] respectively. Especially, the second procedure (Equation 1) seems to be superior for the derivatization of 1-aminoalkanephosphonic acids for the CIMS analysis, since it proceeded selectively with the formation of corresponding volatile N-acylaminoalkanephosphonates **3**.[19]

The representative CIMS spectrum of O,O-dimethyl N-acetylaminoalkanephosphonate **3BA*e**, obtained by derivatization of 1-aminopentanephosphonic acid **1e**

TABLE VI

Reduced chemical ionization mass spectra of O,O-diethyl 1-(trifluoroacetylamino)alkanephosphonates **3CB***

No	R (R'= H)	Molecular formula (mass)	Mass spectrometry: M+1	M - TFA[a] [M-97]	M - NHTFA[b] [M-112]	M - P[c] [M-137]	P[d] [139]
3CB*a	H	$C_7H_{13}F_3NPO_4$	264	166[e]	151	126	
		[263.2]	(100)	(0.3)	(1.1)	(0.4)	(2.0)
3CB*b	CH_3	$C_8H_{15}F_3NPO_4$	278	180[f]	165	140	
		[277.2]	(100)	(0.2)	(0.5)	(2.4)	(4.5)
3CB*c	C_2H_5	$C_9H_{17}F_3NPO_4$	292	194[g]	179	154	
		[291.1]	(100)	(0.2)	(0.6)	(3.2)	(5.0)
3CB*d	CH_3 (CH_3)	$C_9H_{17}F_3NPO_4$	292	194	179	154	
		[291.1]	(100)	(0.2)	(1.5)	(7.2)	(8.2)
3CB*e	n-C_4H_9	$C_{11}H_{21}F_3NPO_4$	320	222[h]	207	182	
		[319.3]	(100)	(<0.1)	(0.4)	(3.5)	(5.0)
3CB*f	C_6H_5	$C_{13}H_{19}F_3NPO_4$	340	242	227[i]	202	
		[339.3]	(100)	(1.0)	(0.7)	(5.0)	(7.0)
3CB*g	$C_6H_5CH_2$	$C_{14}H_{21}F_3NPO_4$	354	256	241[j]	216	
		[353.3]	(100)	(<0.3)	(0.5)	(2.5)	(10.0)

[a] TFA = $CF_3C(O)$-, TFANH = $CF_3C(O)$-NH-, M - P[c] = M - $(EtO)_2POH$, P[d] = $(EtO)_2P(H)OH$, [e]165 (1.0), [f]179 (0.4), [g]193 (0.3), [h]221 (0.3) [i]229 (10.), [j]242 (2.0)

by means of the acetic anhydride—trimethyl orthoacetate system, prior to its mass spectrometric analysis, is presented on Figure 3. Its worth to note that the quasi molecular ion current [M + 1] is identical with the total RIC, and that the derivative **3BA*e** evaporates much faster than the parent amino acid **1e**. The volatility of derivatives **3**, prepared instantly from **1**, can be applied also in their chromatographic separation. The representative chromatogram (GC/CIMS) of the derivatization products of the mixture of **1a–e**, obtained by means of acetic anhydride—trimethyl orthoacetate, prior to their chromatographic analysis is presented on Figure 4. The supplementary chemical ionization mass spectra of this mass spectrometric analysis (GC, see the experimental) are presented on the Figure 4A. The reduced chemical ionization mass spectra of all N-acylaminoalkanephosphonates **3** investigated; N-acetyl-amino (**3BA*** and **3BB***), N-trifluoroacetylamino (**3CA*** and **3CB***), and N-trimethylacetylaminoalkanephosphonates (**3DA*** and **3DB***) are presented in the Tables III–VIII, respectively.

TABLE VII

Reduced chemical ionization mass spectra of O,O-dimethyl 1-(trimethylacetylamino)alkanephosphonates **3DA***

No	R (R'= H)	Molecular formula (mass)	Mass spectrometry: m/z (relative intensity, %)				
			M+1	M - OR [M-31]	M - NHPiv[a] [M-100]	M - P[b] [M-109]	P[c,f] [111]
3DAa	H	$C_8H_{18}NPO_4$	224	192	123[d]	114	
		[223.1]	(100)	(2.7)	(0.3)	(0.2)	(1.1)
3DAb	CH_3	$C_9H_{20}NPO_4$	238	206	137[e]	128	
		[237.1]	(100)	(4.0)	(<0.1)	(7.2)	(2.9)
3DAc	n-C_4H_9	$C_{12}H_{26}NPO_4$	280	248	179	170	
		[279.3]	(100)	(1.8)	(<0.1)	(7.2)	(2.3)
3DAf	C_6H_5	$C_{14}H_{24}NPO_4$	300	268	199	190	
		[299.3]	(100)	(0.6)	(<0.1)	(9.8)	(4.8)
3DAg	$C_6H_5CH_2$	$C_{15}H_{26}NPO_4$	314	282	213	204	
		[313.3]	(100)	(0.8)	(<0.1)	(1.0)	(7.1)

M - PivNH[a] = M - $Me_3CC(O)NH$, M - P[b] = M - $(MeO)_2PO$, P[c] = $(MeO)_2P(H)OH$ [d]166 (0.3), [e]151 (0.3), [f]overlapping with the column background.

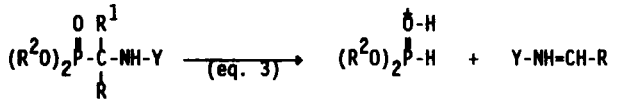
TABLE VIII

Reduced chemical ionization mass spectra of O,O-diethyl 1-(trimethylacetylamino)alkanephosphonates **3DB***

No	R (R'= H)	Molecular formula (mass)	Mass spectrometry:				
			M+1	M - RO [M-45]	M - PivNH[a] [M-100]	M - P[b] [M-137]	P[c] [139]
3DBa	H	$C_{10}H_{22}NPO_4$	252	206	151[d,e]	114	
		[251.2]	(100)	(0.9)	(0.2)	(0.2)	(0.7)
3DBb	CH_3	$C_{11}H_{24}NPO_4$	266	220	165[f]	128	
		[265.2]	(100)	(1.3)	(0.1)	(5.2)	(1.5)
3DBc	n-C_4H_9	$C_{14}H_{30}NPO_4$	308	262	207[g]	170	
		[307.3]	(100)	(0.9)	(0.1)	(8.5)	(2.3)
3DBf	C_6H_5	$C_{16}H_{28}NPO_4$	328	281	227	190	
		[327.3]	(100)	(0.7)	(0.3)	(9.4)	(2.6)
3DBg	$C_6H_5CH_2$	$C_{17}H_{30}NPO_4$	342	295	241	204	
		[341.3]	(100)	(<0.1)	(<0.1)	(2.5)	(4.1)

M - PivNH[a] = M - $Me_3CC(O)NH$, M - P[b] = M - $(EtO)_2P(O)$, P[c] = $(EtO)_2P(H)OH$, [d]152 (0.2), [e]166 (0.3), [f]180 (0.3), [g]223 (0.6).

The main feature of the chemical ionization mass spectra (CI) of these derivatives **3** are: a) the presence of the peaks corresponding to the protonated molecular ions $[M + 1]^+$, b) the formation of the ions corresponding to the loss of the phosphonyl moiety $[M - (R^2O)_2P(O)]^+$, c) the existence of the ions derived from protonated dialkyl phosphites $[(R^2O)_2P{=}OH(H)]^+$, formed according to Equation 3:



In case of higher homologs of derivatives **3** (e.g. **3e–g**) the ions $[R{-}CH{=}NH_2]^+$

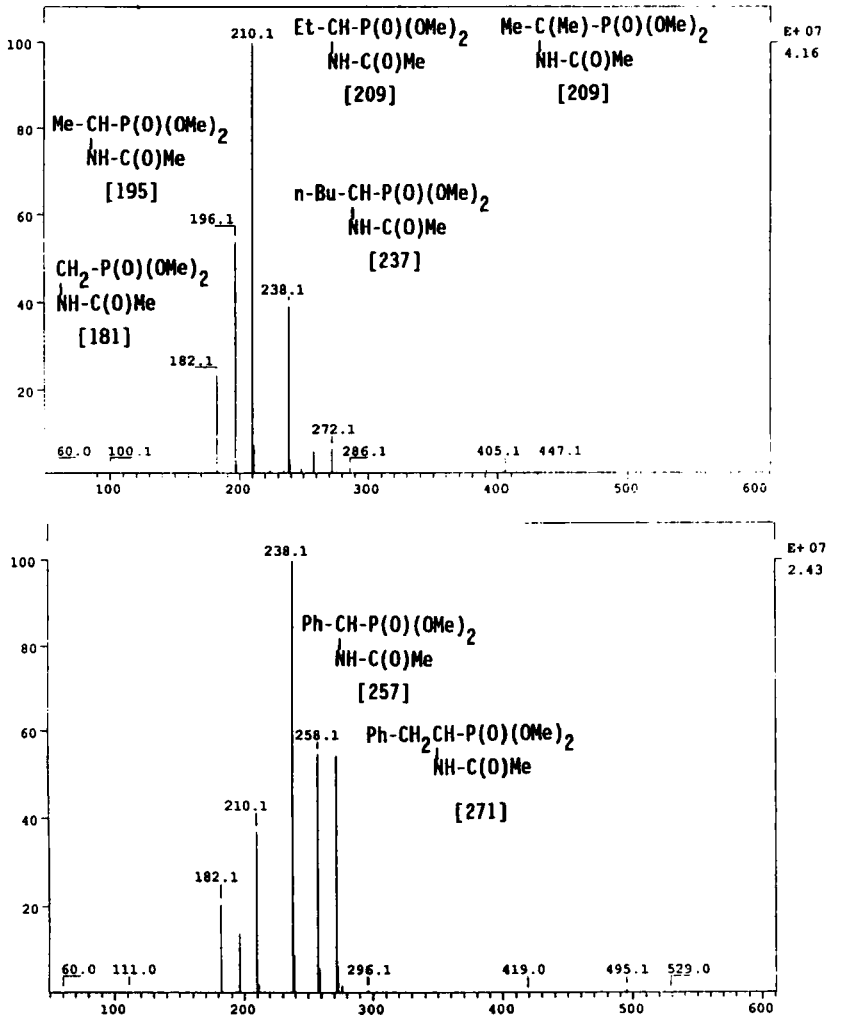


FIGURE 5 Isobutane chemical ionization mass spectra (CI) of the mixture of O,O-dimethyl 1-(N-acetylamino)alkanephosphonates **3BA*** obtained by the derivatization of the mixture of 1-aminoalkanephosphonic acids **1a**, **1b**, **1c**, **1d**, **1e**, **1f** and **1g**, by means of the acetic anhydride-trimethyl orthoformate system.

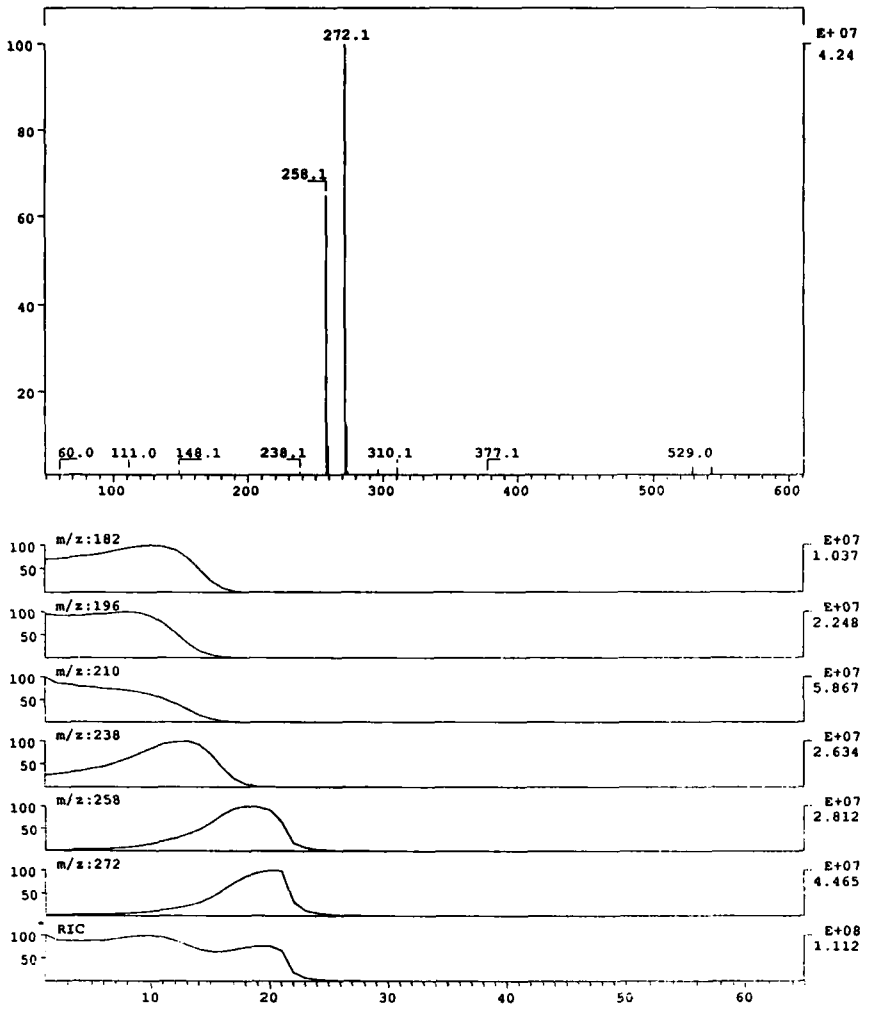


FIGURE 5 (*Continued*)

related to the imine structure have also been observed in the corresponding CIMS spectra.

The Application of Chemical Ionization Mass Spectrometry for the Analysis of the Mixture of 1-aminoalkanephosphonic Acids

The analysis of the mass spectral properties (GC/CIMS, CIMS) of the derivatives **3** (Figure 3 and 4A, and Tables III–VIII) indicates that these compounds can be applied in the chemical ionization mass spectrometry for the analysis of the multi-component mixture of the parent 1-aminoalkanephosphonic acids **1**. The mass spectra (CI) of N-acetyloaminoalkanophosphonates **3BA*a–g** obtained by the derivatization of the mixture of the 1-aminoalkanephosphonic acids **1a–g** are pre-

sented on the Figure 5. The evaporation mode of the mixture of derivatives **3BA*** indicates the possibility of their gradual fractionation during the evaporation.

CONCLUSIONS

The application of the chemical ionization mass spectrometry using isobutane as a reacting gas for the analysis (structural and quantitative) of underivatized 1-aminoalkanephosphonic acids **1** presents a moderate value. However, the conversion of unvolatile free amino acids **1** into their corresponding O,O-dialkyl N-acylaminoalkanephosphonates **3**, prior to their mass spectrometric analysis (GC/CIMS or/or CIMS), represents the powerful tool in the analysis of this class of compounds. The derivatives **3** are volatile and simplicity of their mass spectra (CIMS) allows the application of these techniques for the analysis of the whole class of aminoalkanephosphonic acids.

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