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Matrix-assisted ultraviolet laser desorption/ionization time-of-flight (UV-MALDI-TOF) mass spectra of N-acylated and N,O-acylated glycosylamines

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Abstract—Matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectrometry (UV-MALDI-TOF-MS) has shown to be a very useful technique for the study of the non-volatile and thermally non-stable N-acylated glycopyranosyl- and glycofuranosyl-amines. Of the several matrices tested, 2,5-dihydroxybenzoic acid (DHB) was the most effective giving good spectra in the positive-ion mode. In the linear and reflectron modes, the $[M+Na]^+$ ions appeared with high intensity. Their fragmentation patterns were investigated by post-source decay (PSD) UV-MALDI-TOF-MS showing mainly cross-ring cleavages.

In addition, N,O-acylated glycopyranosyl- and glycofuranosyl-amines were also analyzed by this technique. PSD UV-MALDI-TOF-MS gave significant signals for several primary fragment ions, which were proposed but not detected, or observed with very low abundance, in electron ionization mass spectrometry (EI-MS) experiments.

Keywords: N-Acylated glycosylamines; N,O-Acylated glycosylamines; UV-MALDI-TOF-MS; PSD UV-MALDI-TOF-MS

1. Introduction

Matrix-assisted ultraviolet laser desorption/ionization mass spectrometry (UV-MALDI-MS) has become a major technique for carbohydrate analysis since its introduction to the field[1] in 1991, with a steady year-by-year increase in reports.[2–6] It is apparent from the work covered in recent reviews[2–6] that, as the technique matures, greater emphasis has been placed on applications rather than on fundamental aspects and method development.

A number of options are available for obtaining fragmentation spectra from carbohydrates ionized by UV-MALDI[5] and derivatization of carbohydrates may be used especially for improving sensitivity and simplifying fragmentation. Thus, the effect of peracetylation and perbenzoylation has been studied,[2–6] but there is little knowledge related to the fragmentation pathways of these derivatives, which sometimes causes uncertainty in finding diagnostic ions for structural information.

The most common derivatization technique for reducing sugars is reductive amination. However, recent studies[7] by electrospray-ionization mass spectrometry suggest that closed-ring N-derivatives (*N*-acylglycosylamines) could provide greater structural information on linkage than open-ring products. Glycosylamines belong to an important group of biologically active compounds.

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Many of them include nucleic acids, glycoproteins, coenzymes, some of the members of the vitamin B group, etc.

Herein we report the application of UV-MALDI-TOF-MS and PSD UV-MALDI-TOF-MS for the analysis of several N-acylated glycosylamines. In addition, N,O-acylated glycosylamines were also analyzed by the same techniques and the results are compared with those obtained previously by EI-MS.[8,9]

2. Experimental

2.1. Materials

2.1.1. Matrices for UV-MALDI-TOF-MS. The β-carboline 9*H*-pyrido[3,4-*b*]indole or *nor*-harmane was purchased from Sigma–Aldrich. Classical matrix compounds: 2,5-dihydroxybenzoic acid (DHB, gentisic acid), 2,4,6-trihydroxyacetophenone (THAP), 2-(4-hydroxyphenylazo)benzoic acid (HABA), 3-indoleacrylic acid (IAA), 6-aza-2-thiothymine (2-ATT), and 5-chloro-2-mercaptobenzothiazole (CMBT) were purchased from several sources (Sigma–Aldrich, Acros Organics, Nacalai Tesque, Inc., Japan).

2.1.2. Calibration standards. Positive-ion mode: α-cyclodextrin (cyclohexaamylose, MW 972.9) and neoagarobiose (MW 324.3). Negative-ion mode: α-cyclodextrin (MW 972.9) and neocarrabiose 4′-sulfate sodium salt (MW 426.3). Chemicals were obtained from Sigma–Aldrich.

2.1.3. Organic solvents. MeOH and THF (Sigma–Aldrich, HPLC grade), were used as purchased without further purification. EtOH was provided by Nacalai Tesque, Inc. (Japan). Water of very low conductivity (Milli Q grade; 56–59 nS/cm with PURIC-S, ORUGANO Co., Ltd, Tokyo, Japan) was used.

2.2. UV-MALDI-TOF-MS

2.2.1. Instruments. Measurements were performed using: (a) a Shimadzu Kratos, Kompact MALDI 4 (pulsed extraction) laser desorption time-of-flight mass spectrometer (Shimadzu, Kyoto, Japan), (b) an Applied Biosystems Voyager DE-STR laser desorption time-of-flight mass spectrometer, both equipped with pulsed nitrogen laser ($\lambda_{em} = 337$ nm; pulse width = 3 ns), tunable pulsed-delayed extraction (PDE) and post-source decay (PSD MS/MS device) modes, as described elsewhere.[10–15]

Experiments were performed using first the full range setting for laser firing position to select the optimal position for data collection, and secondly fixing the laser firing position in the sample sweet spots. The samples were irradiated just above the threshold laser power for obtaining molecular ions and with higher laser power for studying cluster formation. Thus, the irradiation used for producing a mass spectrum was analyte-dependent. Usually 50 spectra were accumulated. The sample was measured in the linear and reflectron modes, in both positive- and negative-ion modes.

2.2.2. Probe supports. The stainless steel polished surface twenty-sample slides were purchased from Shimadzu Co., Japan (P/N 670-19109-01). Polished surface slides were used to get better images for morphological analysis with a stereoscopic microscope (NIKON Optiphot, Tokyo, Japan; magnification ×400) and with a high-resolution digital microscope (Keyence VH-6300, Osaka, Japan; magnification ×800). Gold sample plates (199 well, P/N V700401) were used in the Applied Biosystems Voyager DE-STR mass spectrometer. Samples were placed at locations, which were mirror-polished.

2.2.3. Sample preparation. Analyte solutions were freshly prepared by dissolving the carbohydrates (1 mg) in pure water (0.5 mL). Matrix solutions were made by dissolving 2–10 mg of the selected compound in 1 mL of the proper solvent. Sometimes matrix-saturated solutions were used. For DHB and *nor*-harmane, the matrix solutions were prepared in 1:1 (v/v) MeOH–H_2O. For IAA and HABA, the matrix solutions were prepared in THF. 2-ATT was prepared in H_2O.

To prepare the analyte/matrix deposit two methods were used. Method A (sandwich method) and Method B (mixture method). In the former, 0.5 μL of the matrix solution was placed on the sample probe tip and the solvent was removed by blowing air at room temperature. Subsequently, 0.5 μL of the analyte solution was placed on the same probe tip, covering the matrix and partially dissolving it. After drying by blowing air, two additional portions (0.5 μL) of the matrix solution were deposited on the sample probe tip, producing a partial dissolution of the previously deposited thin-film matrix and analyte layers. In Method B, the analyte stock solution was mixed with the matrix solution in 1:1 to 1:8 (v/v) ratios. A 0.5 μL aliquot of this analyte/matrix solution was deposited onto the probe tip and dried with a stream of forced room temperature air. Then, an additional portion of 0.5 μL was applied to the dried solid layer on the probe, causing it to redissolve partially, and the solvent was removed by blowing air.

For combination of CMBT and DHB as matrix, CMBT was dissolved in 1:1:1 (v/v/v) THF–EtOH–H_2O and DHB was dissolved in H_2O. In the sample preparation method, a saturated droplet (1 μL) of CMBT was deposited on the sample probe tip. The solvent was removed by blowing air and 1 μL of analyte solution was placed on the same probe tip dissolving partially the CMBT layer. After drying, 1 μL of the DHB water solution was transferred on the probe.

2.2.4. Spectrum calibration. Spectra were calibrated by use of external calibration reagents in both positive and negative linear and reflectron modes. The Kratos Kompact calibration program and the Voyager DE-STR calibration program were, respectively, used.

3. Results and discussion

Table 1 shows the different N-acylated glycosylamines (compounds **1**–**4**) and N,O-acylated glycosylamines (compounds **5**–**7**) that were analyzed by UV-MALDI-TOF-MS in linear and reflectron positive-ion and negative-ion modes. As part of an on-going comparative study on the behavior of different compounds as UV-MALDI matrices for carbohydrate analysis,[10–15] several matrices (*nor*-harmane, DHB, THAP, HABA, IAA, 2-ATT, and CMBT) and sample preparation methods were evaluated. Spectra of better quality were obtained in positive-ion mode with DHB and *nor*-harmane using method A (sandwich method) for sample preparation; the ratio of satellite-adduct signal intensity to molecular ion signal intensity was negligible for both matrices. Signals of higher absolute intensity (expressed in mV) and higher signal-to-noise ratio were obtained when samples were prepared with DHB. In addition, the distribution of the sweet spots was more homogeneous and each sweet spot surface was larger.

As for the other matrices, with THAP, all the compounds studied gave spectra similar to those obtained with DHB and *nor*-harmane, although at quite minor signal-to-noise ratio; no clusters or significant satellite signals were observed. On the contrary IAA gave a quite significant amount of clusters, together with satellite signals close to the molecular ion peaks. 2-ATT and CMBT, both matrices characterized by their mild acid character, were used combined with DHB, a stronger acid, to check if desorption/ionization efficiency could be better than with DHB alone. No significant improvement was observed. Finally, the HABA matrix yielded weak molecular ion signals only for peracetylated glycosylamines **5**–**7**. Thus, PSD experiments were conducted only with DHB and *nor*-harmane. Similar fragmentation patterns were obtained with both matrices being of higher quality the spectra obtained with DHB.

3.1. UV-MALDI-TOF-MS of compounds 1–4

Compounds **1**–**4**, as expected, show only the signal of the sodiated molecular ion in linear and reflectron positive-ion modes. Table 2 shows the fragment ions observed in the PSD UV-MALDI-TOF mass spectra with DHB as matrix. Generally, in these mass spectra cross-ring cleavages of the sodiated molecular ion were observed. These cross-ring cleavages are similar to those previously reported[16] in FAB-MS/MS of lithiated disaccharides.

Table 2. Most important peaks observed in the positive-ion mode PSD UV-MALDI mass spectra of N-acylated glycosylamines **1**–**4**

Compound	*m*/*z*	Assignment
1	214.1	$[M+Na]^+$
	202.4	$([M+Na]+H_2O-HCHO)^+$
	181.0	$([M+Na]-HOO)^{+\cdot}$
	154.0	$([M+Na]-HOCH_2CHO)^+$
	131.0	$([M+Na]-Na-HOCH_2CHO)^{+\cdot}$
	130.0	NA[a]
	124.1	$([M+Na]-HOCH_2COH{=}CHOH)^+$
	113.0	$([M+Na]-HOHC{=}CHNHCOCH_3)^+$
	88.9	NA
2	244.3	$[M+Na]^+$
	226.3	$([M+Na]-H_2O)^+$
	224.3	NA
	154.2	$([M+Na]-HOCH_2COH{=}CHOH)^+$
	143.3	$([M+Na]-HOHC{=}CHNHCOCH_3)^+$
	124.1	$([M+Na]-HOCH_2CHOHCOH{=}CHOH)^+$
3	244.2	$[M+Na]^+$
	226.2	$([M+Na]-H_2O)^+$
	197.1	$([M+Na]+H_2O-Na-CH_2CO)^{+\cdot}$
	185.1	$([M+Na]-CH_3CONH_2)^+$
	154.1	$([M+Na]-HOCH_2COH{=}CHOH)^+$
	143.2	$([M+Na]-HOHC{=}CHNHCOCH_3)^+$
	124.0	$([M+Na]-HOCH_2CHOHCOH{=}CHOH)^+$
4	276.3	$[M+Na]^+$
	258.3	$([M+Na]-H_2O)^+$
	245.2	NA
	216.2	$([M+Na]-HOCH_2CHO)^+$
	186.1	$([M+Na]-HOCH_2COH{=}CHOH)^+$
	159.0	$([M+Na]-HOCH_2COH{=}CHOH-HCN)^+$
	144.1	$[C_6H_5CONH_2+Na]^+$
	113.1	$([M+Na]-HOHC{=}CHNHCOC_6H_5)^+$

[a] NA = not assigned.

Table 1. List of the acylated glycosylamines analyzed in this study

Compound	Name	Molecular weight
1	*N*-Acetyl-β-D-xylopyranosylamine	191.2
2	*N*-Acetyl-α-D-galactopyranosylamine	221.2
3	*N*-Acetyl-α-D-glucofuranosylamine	221.2
4	*N*-Benzoyl-β-D-xylopyranosylamine	253.2
5	*N*-Acetyl-2,3,4-tri-*O*-acetyl-α-L-arabinopyranosylamine	317.3
6	*N*-Acetyl-2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosylamine	389.3
7	*N*-Acetyl-2,3,5,6-tetra-*O*-acetyl-α-D-glucofuranosylamine	389.3

Thus, in the spectrum of compound **1** (Fig. 1, Scheme 1), the elimination of formaldehyde, due to the cleavage of linkages 0 and 4 (numbering according to the nomenclature of Domon and Costello)[17] gave the hydrated fragment at *m*/*z* 202.4. The signal at *m*/*z* 154.0, which derives from a ^{0,3}X fragmentation involves loss of glycolaldehyde, whereas the peak at *m*/*z* 124.1 corresponds to a ^{0,2}X cleavage with elimination of $C_3H_6O_3$. On the other hand, retention of the charge on the latter (^{0,2}A fragmentation) leads to the signal at *m*/*z* 113.0. In addition, fragmentation involving possible elimination of the HOO radical (*m*/*z* 181.0) was detected, and the signal at *m*/*z* 131.0 (radical ion) was tentatively ascribed to a fragment without sodium; radical ion species have been already reported[18] in MALDI-TOF-MS experiments.

For compounds **2** (a hexopyranosylamine) and **3** (a hexofuranosylamine), similar fragmentation pathways were observed. Thus, these compounds eliminated, as expected, $C_3H_6O_3$ (^{0,3}X fragmentation, *m*/*z* 154.2–154.1) and $C_4H_8O_4$ (^{0,2}X fragmentation, *m*/*z* 124.1–124.0). The signal at *m*/*z* 143.3–143.2 was consistent with a ^{0,2}A fragmentation which led, by loss of 2-ace-

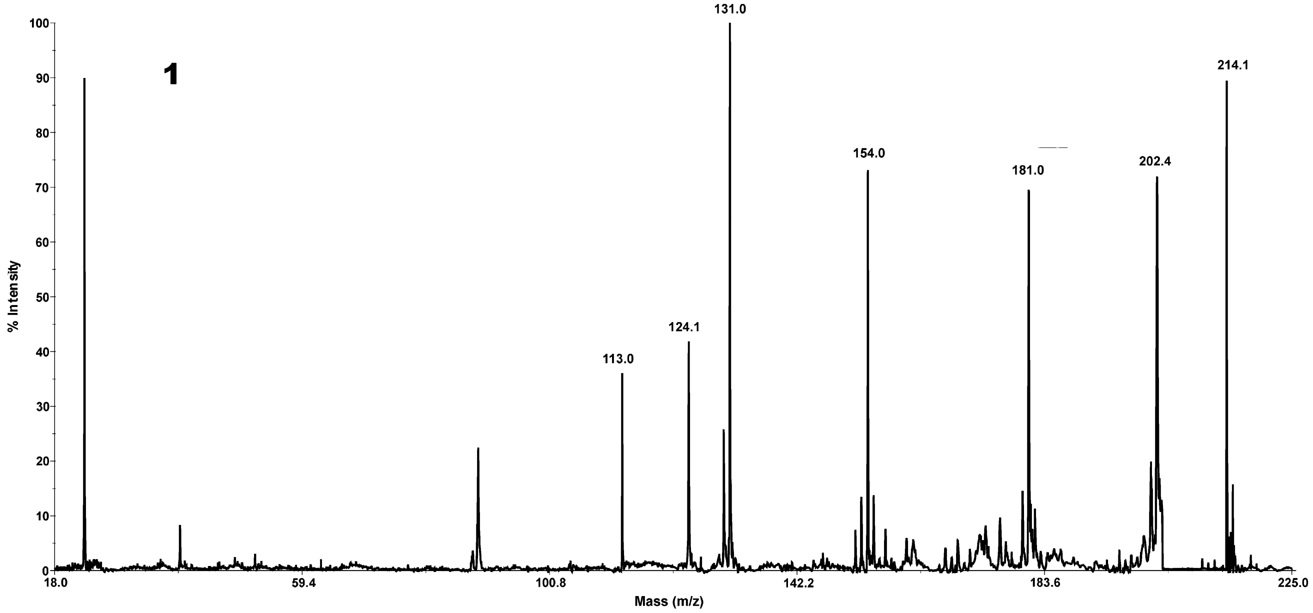
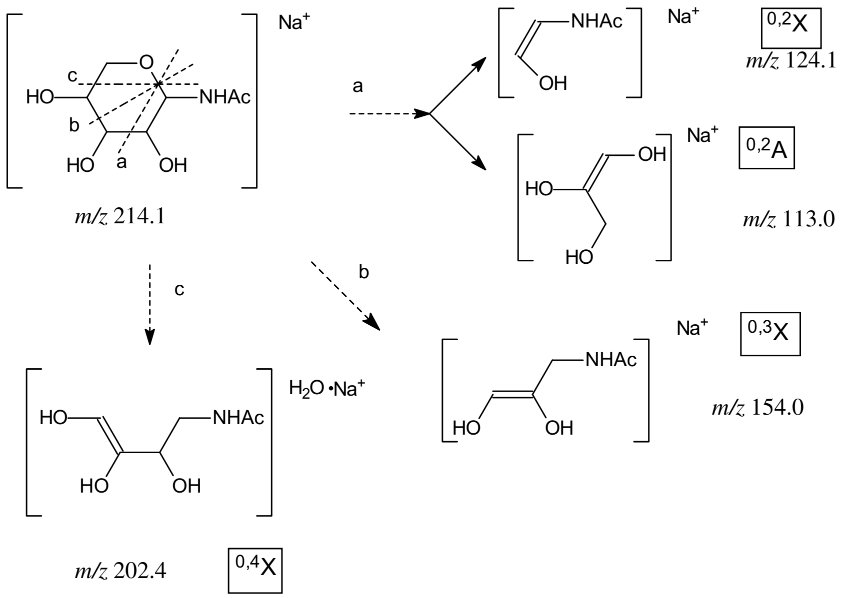


Figure 1. PSD UV-MALDI-TOF mass spectrum of compound **1** (*λ*: 337 nm, positive-ion mode, matrix: DHB).



Scheme 1.

tamidoethanal, to $C_4H_8O_4$ cationized with sodium. In the spectrum of compound **3** the *N*-acetyl group was eliminated as acetamide (*m*/*z* 185.1) or ketene (*m*/*z* 197.1); the latter signal was tentatively ascribed to a radical ion.

As shown in Table 2, a clear fragmentation pattern occurred for compound **4** losing glycolaldehyde (^{0,3}X fragmentation, *m*/*z* 216.2) or $C_3H_6O_3$ (^{0,2}X fragmentation, *m*/*z* 186.2). All the signals kept the sodium cation and no peaks corresponding to fragments without sodium were detected. After losing $C_3H_6O_3$, the remaining fragment released a molecule of hydrogen cyanide to give an important signal at *m*/*z* 159.0. The peaks corresponding to benzamide cationized with sodium (*m*/*z* 144.1) and to a ^{0,2}X fragmentation (*m*/*z* 113.1) were also found.

3.2. UV-MALDI-TOF-MS of compounds 5–7

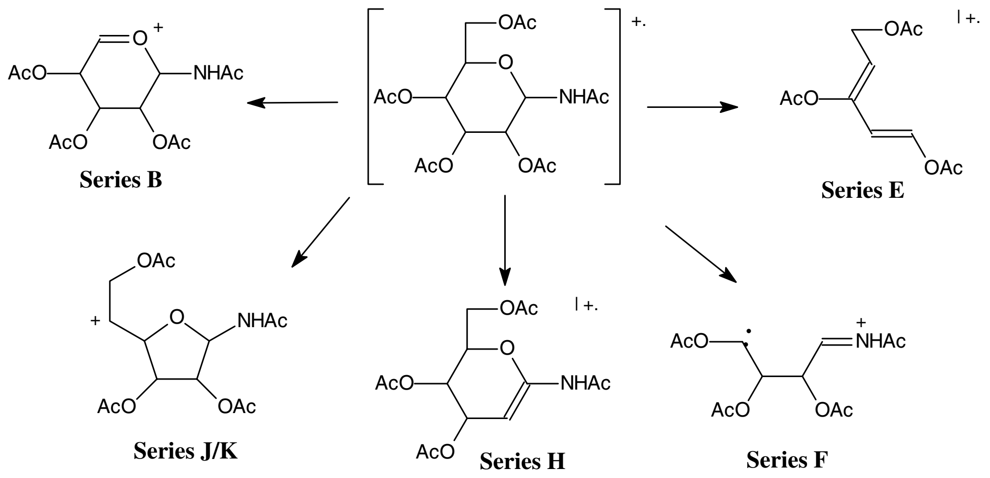
In linear and reflectron positive-ion modes, compounds **5**–**7** show mainly the signal $[M+Na]^+$ and, as a minor process, the loss of one (in some cases two) molecule of ketene from the sodiated molecular ion. The EI mass spectra of acetylated and propanoylated aldopyranosyl- and aldofuranosyl-amines have been previously reported[8,9] and several fragmentation pathways were recognized (Series A–K). Even though the primary fragments, shown in Scheme 2, were proposed as first steps of fragmentation for acetylated hexopyranosylamines, they were only detected with low abundance, or not detected, giving rise to signals of higher intensity by further loss of neutral molecules.

Table 3 shows the fragment ions observed in the PSD UV-MALDI-TOF-MS with DHB as matrix. The spectrum of compound **5** (molecular ion peak $[M+Na]^+$, *m*/*z* 340.2), shows an intense fragment (*m*/*z* 280.2) due to the loss of acetic acid and two minor signals produced by successive elimination of another molecule of acetic acid (*m*/*z* 220.1) and ketene (*m*/*z* 178.0). The peak of high intensity at *m*/*z* 258.2 may be attributed to the loss of Na^+ followed by elimination of acetate; further elimination of ketene gives rise to the intense signal at *m*/*z* 216.2, whereas consecutive loss of two molecules of acetic acid produces small signals at *m*/*z* 198.9 and 138.0.

A similar pattern of fragmentation (Scheme 3) was observed for compound **6**. Thus the sodiated molecular ion mainly follows fragmentation pathways equivalent to series H and K, described before in EI-MS.[8] However, whereas in EI-MS loss of ketene was only observed after elimination of acetic acid (series K), in the PSD spectra of compounds **5** and **6** ketene was expelled in a first step giving important signals at *m*/*z* 216.2 and 288.1, respectively. Loss of acetic acid from the molecular ion of compound **6** followed by decomposition by a retro Diels–Alder reaction led to an important signal at *m*/*z* 265.1.

For compound **6**, successive loss of acetic acid and ketene (*m*/*z* 310.0) from the molecular ion is equivalent to the shedding of the acetate of glycolaldehyde (2-acetoxyethanal, series F). Analysis of the corresponding N,O-propanoylated derivative (data not shown) supports that the peak at *m*/*z* 310.0 would be mainly due to the elimination of the acetate of glycolaldehyde.

It is important to note that in the PSD spectra of compounds **5** and **6** intense peaks were observed at high *m*/*z* values, a region where no important signals were found in the corresponding EI spectra. It has been previously reported[6,19] that protonation of an oligosaccharide is likely to be localized on the glycosidic oxygen; on the other hand, metal ions can undergo coordination with several atoms simultaneously, resulting in less destabilization of the glycosidic bond. Our results



Scheme 2.

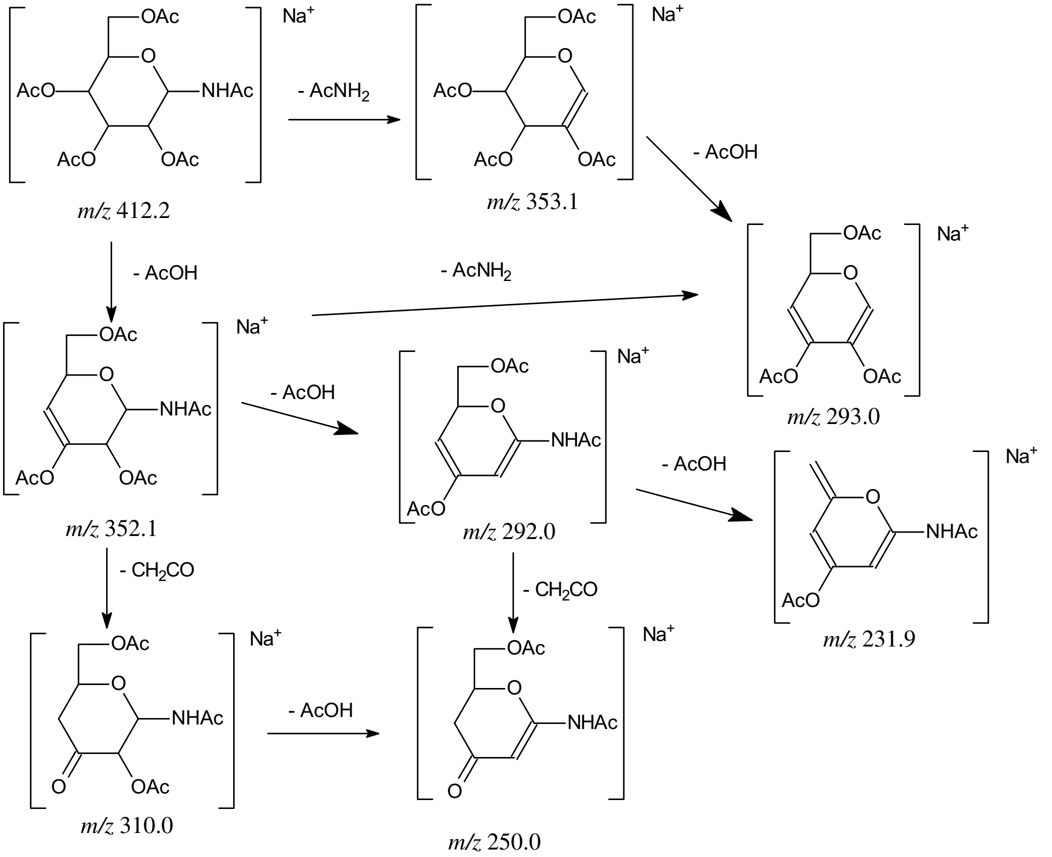
Table 3. Fragmentations observed in the positive-ion mode PSD UV-MALDI mass spectra of peracetylated glycosylamines **5**–**7**

Compound	*m*/*z*	Assignment	Series
5	340.2	$[M+Na]^+$	
	280.2	$([M+Na]-CH_3CO_2H)^+$	H
	258.2	$([M+Na]-Na-CH_3CO_2)^+$	K
	220.1	$([M+Na]-2CH_3CO_2H)^+$	H
	216.2	$([M+Na]-Na-CH_3CO_2-CH_2CO)^+$	K
	203.0	NA[a]	
	201.5	NA	
	198.9	NA	
	178.0	$([M+Na]-2CH_3CO_2H-CH_2CO)^+$	H
		$([M+Na]-CH_3CO_2CH_2CHO-CH_3CO_2H)^+$	F
	138.0	$([M+Na]-Na-CH_3CO_2-2CH_3CO_2H)^+$	K
6	412,2	$[M+Na]^+$	
	353.1	$([M+Na]-CH_3CONH_2)^+$	H
	352.1	$([M+Na]-CH_3CO_2H)^+$	E, H
	330.1	$([M+Na]-Na-CH_3CO_2)^+$	K
	310.0	$([M+Na]-CH_3CO_2H-CH_2CO)^+$, $([M+Na]-CH_3CO_2CH_2CHO)^+$	F, H
	293.0	$([M+Na]-CH_3CO_2H-CH_3CONH_2)^+$	H
	292.0	$([M+Na]-2CH_3CO_2H)^+$	H
	288.1	$([M+Na]-Na-CH_3CO_2-CH_2CO)^+$	K
	270.0	$([M+Na]-Na-CH_3CO_2-CH_3CO_2H)^+$	K
	265.1	$([M+Na]-CH_3CO_2H-CH_3CONHCHO)^+$	E
	250.0	$([M+Na]-2CH_3CO_2H-CH_2CO)^+$	H
		$([M+Na]-CH_3CO_2CH_2CHO-CH_3CO_2H)^+$	F
	246.0	$([M+Na]-Na-CH_3CO_2-2CH_2CO)^+$	K
	231.9	$([M+Na]-3CH_3CO_2H)^+$	H
	229.0	$([M+Na]-Na-CH_3CO_2-CH_3CONH_2-CH_2CO)^+$	K
	228.0	$([M+Na]-Na-CH_3CO_2-CH_3CO_2H-CH_2CO)^+$	K
	211.0	$([M+Na]-Na-CH_3CO_2-CH_3CO_2H-CH_3CONH_2)^+$	K
	210.0	$([M+Na]-Na-CH_3CO_2-2CH_3CO_2H)^+$	K
	186.4	$([M+Na]-Na-CH_3CO_2-CH_3CO_2H-2CH_2CO)^+$	K
	168.9	$([M+Na]-Na-CH_3CO_2-CH_3CO_2H-CH_3CONH_2-CH_2CO)^+$	K
	167.9	$([M+Na]-Na-CH_3CO_2-2CH_3CO_2H-CH_2CO)^+$	K
7	412.2	$[M+Na]^+$	
	352.2	$([M+Na]-CH_3CO_2H)^+$	H
	330.2	$([M+Na]-Na-CH_3CO_2)^+$	K
	310.1	$([M+Na]-CH_3CO_2H-CH_2CO)^+$	H
	292.1	$([M+Na]-2CH_3CO_2H)^+$	H
	288.1	$([M+Na]-Na-CH_3CO_2-CH_2CO)^+$	K
	270.1	$([M+Na]-Na-CH_3CO_2-CH_3CO_2H)^+$	K
	269.1	$([M+Na]-CH_3CONH_2-2CH_2CO)^+$	H
		$([M+Na]-(CH_3CO_2)CHCHNHCOCH_3)^+$	
	251.3	$([M+Na]-CH_3CO_2H-CH_3CONH_2-CH_2CO)^+$	H
	250.4	$([M+Na]-2CH_3CO_2H-CH_2CO)^+$	H
		$([M+Na]-CH_3CO_2CH_2CHO-CH_3CO_2H)^+$	F
	246.4	$([M+Na]-Na-CH_3CO_2-2CH_2CO)^+$	K
	232.0	$([M+Na]-3CH_3CO_2H)^+$	H
	229.1	$([M+Na]-Na-CH_3CO_2-CH_3CONH_2-CH_2CO)^+$	K
	228.1	$([M+Na]-Na-CH_3CO_2-CH_3CO_2H-CH_2CO)^+$	K
	210.0	$([M+Na]-Na-CH_3CO_2-2CH_3CO_2H)^+$	K
	187.3	$([M+Na]-Na-CH_3CO_2-CH_3CONH_2-2CH_2CO)^+$	K
	186.3	$([M+Na]-Na-CH_3CO_2-CH_3CO_2H-2CH_2CO)^+$	K
	169.0	$([M+Na]-Na-CH_3CO_2-CH_3CO_2H-CH_3CONH_2-CH_2CO)^+$	K
	168.0	$([M+Na]-Na-CH_3CO_2-2CH_3CO_2H-CH_2CO)^+$	K
	150.0	$([M+Na]-Na-CH_3CO_2-2CH_3CO_2H-CH_2CO-CO)^+$	K

[a] NA = not assigned.

suggest that Na^+ could also stabilize the molecule of a peracylated glycosylamine leading, in consequence, to less fragmentation.

For compound **7**, an acylated hexofuranosylamine, only fragments corresponding to series H and K were detected. This observation is consistent with the previous results[9] reported in EI-MS of acylated aldofuranosylamines where: (a) series H and K gave rise to some peaks of high intensity, (b) series F was of little importance, and (c) series E involving the retro-Diels–Alder



Scheme 3.

reaction did not occur because the latter is not possible for a five-membered ring.

4. Conclusions

UV-MALDI-TOF-MS has shown to be a very useful technique for the study of the non-volatile and thermally non-stable monosaccharide derivatives **1**–**4** (N-acylated glycosylamines). In the linear and reflectron modes the $[M+Na]^+$ ions appeared with high intensity while in the PSD mode cross-ring cleavages were the main fragmentation pathways for these compounds.

Several primary fragment ions not found, or detected with very low abundance, in EI-MS of compounds **5**–**7** (peracylated glycosylamines) were clearly observed in the present study by PSD UV-MALDI-TOF-MS. Thus, the fragmentation pathways and the intermediates previously proposed[8,9] were confirmed. The fact that the fragmentation pathways in the PSD mode were similar to those reported in EI-MS, suggests that these fragmentation processes are not affected by the nature of the molecular ion, that is, a sodium cationized species $[M+Na]^+$ in the former and a radical cation $[M]^{+\cdot}$ in the latter. In both cases, the vibrationally excited species formed $([M]^{+\cdot})^v$ and $([M+Na]^+)^v$ suffer similar cleavage: the former yields a vibrationally excited intermediate $[I_1]$, which further decomposes into stable ionic fragments of lower m/z value; the latter gives the equivalent sodiated species $[I_1+Na]^+$ as a detectable stable primary ion. Furthermore, molecular ions as $[M+Na]^+$ species were always detected as high intensity signals in the linear and reflectron mass spectra of these compounds. It has been reported[5] that fragmentation patterns obtained by MALDI-MS of carbohydrates are similar to those obtained with other methods of ionization. As fragmentation processes for each family of derivatized glycosylamines was almost fully interpreted, this knowledge will shed some light on the spectral analysis of higher molecular weight N-acylated and N,O-acylated carbohydrates by MS/MS UV-MALDI-TOF-MS.

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