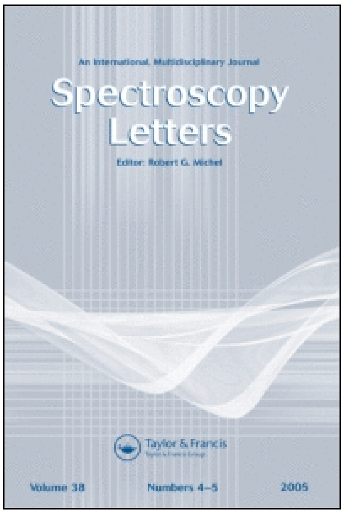

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Mass Spectrometry of Oligosaccharides(I)—Formation of the $[M+Nh_4]^+$ Ion of Oligosaccharides in Fast Atom Bombardment Mass Spectrometry

Panl Yuan-Jiang[a]; Zhai Jian-Jun[b]; Chen Yao-Zu[ab]
[a] Department of Chemistry, Zhejiang University, Hangzhou, P.R.China [b] The state key Laboratory of Applied Organic Chemistry, Lanzhou University, P.R.China

To cite this Article Yuan-Jiang, Panl , Jian-Jun, Zhai and Yao-Zu, Chen(2000) 'Mass Spectrometry of Oligosaccharides(I)—Formation of the $[M+Nh_4]^+$ Ion of Oligosaccharides in Fast Atom Bombardment Mass Spectrometry', Spectroscopy Letters, 33: 4, 469 — 473

To link to this Article: DOI: 10.1080/00387010009350131
URL: http://dx.doi.org/10.1080/00387010009350131

SPECTROSCOPY LETTERS, 33(4), 469–473 (2000)

MASS SPECTROMETRY OF OLIGOSACCHARIDES(I)—FORMATION OF THE $[M+NH_4]^+$ ION OF OLIGOSACCHARIDES IN FAST ATOM BOMBARDMENT MASS SPECTROMETRY

Keywords: Mass Spectrometry, Fast Atom Bombardment MS, Oligosaccharides, FAB-MS

Yuan-Jiang Pan[1*] Jian-Jun Zhai [2] Yao-Zu Chen [1,2]

[1]Department of Chemistry, Zhejiang University Hangzhou 310027, P.R.China
[2]The state key Laboratory of Applied Organic Chemistry, Lanzhou University, 730000, P.R.China

ABSTRACT

In positive-ion fast atom bombardment (FAB) mass spectrometry, when oligosaccharides are mixed with an appropriate amount of NH_4Cl, a highly abundant $[M+NH_4]^+$ peak appears in FAB mass spectra. From the adduct ion $[M+NH_4]^+$, the molecular weights of oligosaccharides can be determined definitively. This technique may especially be applied to analyze the mixture of oligosaccharides.

*Corresponding Author. Fax: +86 571 7951358

INTRODUCTION

Fast atom bombardment (FAB) ionization has been shown to be a very useful method in the mass spectrometric analysis of a wide range of natural compounds, such as glycosides, saccharides, antibiotics, and other highly polar compounds[1]. However, although FAB itself can provide relative molecular mass information of glycosides and saccharides, the low abundance of $[M+H]^+$ ions and chemical noise from the background of the FAB matrix greatly limit the molecular mass information.

Fenselau *et al* [2] and Takayama et al[3] had reported that the FAB spectra of complex organic compounds, such as glycosides showed intense peaks corresponding to ammonium or alkali metal cationized species, $[M+C]^+$($C=NH_4$, Na, K, etc.).This technique is often applied to determine the molecular weights of glycosides [4-6].

Positive-FAB provides less information on molecular weights of oligosaccharides because of the low abundance of $[M+H]^+$ ions, the determination of the molecular weights of oligosaccharides is usually carried out by negative ion FAB[7]. Rollgen et al[8] reported the adduct ions $[M+C]^+$ of mono-saccharides, [C=Li, Na, K] in field desorption mass spectrometry (FD-MS), which provided the molecular weight information.

In this paper, we report the results of a study of $[M+NH_4]^+$, of some mono-saccharides, disaccharides, and their mixtures. We have observed significant enhancement of the relative abundance of mono- or di-saccharides pseudo-molecular ions by the addition of some amount of NH_4Cl into the FAB matrix. Using this technique, the molecular weights of oligosaccharides may easily be determined by positive FAB mass spectrometry.

EXPERIMENTAL

The FAB mass spectra were obtained on a VG ZAB-HS mass spectrometer fitted with a VG 11/250 data system. Argon (99.9%) was used as the target gas of the fast atom gun. The sputtered ions were extracted and accelerated with a potential of 8 kV (1 mA). All the samples were analyzed by dissolving them in water and mixing about

TABLE 1
The relative abundance of $[M+H]^+$ and $[M+NH_4]^+$ of compounds 1-17

Compound	$[M+H]^+$(%)	$[M+NH_4]^+$ (%)
1	181(<2)	198(70)
2	181(<2)	198(100)
3	181(<2)	198(32)
4	165(<2)	182(73)
5	181(<2)	198(95)
6	151(<2)	168(30)
7	151(<2)	168(90)
8	151(<2)	168(100)
9	135(<2)	152(62)
10	343(<1)	360(20)
11	343(<1)	360(30)
12	343(<1)	360(5)
13	343(<1)	360(31)
14	343(<1)	360(15)
15	181(<2)	198(31)
16	123(32)	140(98)

1~2ul of the solution into 1~2ul of matrix (glycerol), adding 0.5~1.0 ul saturated solution of NH_4Cl.

The following compounds were analysed: 1. glucose, 2. fructose, 3. galactose, 4. rhamnose, 5. mannose , 6. arabinose, 7. xylose, 8. ribose, 9. 2-desoxyribose, 10.trehalose, 11.maltose,12.cellobiose,13.sucrosoe,14.lactose, 15.meso-inositol, 16. meso-erythritol 17. glucose+ rhamnose; 18. fructose + rhamnose, 19. glucose+ arabinose, 20. fructose + maltose; 21. Rhamnose + maltose 22. glucose + arabinose + rhamnose ; 23 glucose + arabinose + maltose , 24. Rhamnose + fructose + maltose.

RESULTS AND DISCUSSION

The abundance of $[M+H]^+$, and $[M+NH_4]^+$ of samples 1-17 is presented in Table 1. From the FAB data, it can be seen that there is a higher abundance of $[M+NH_4]^+$ peak, than that of $[M+H]^+$ peak with addition of NH_4^+ to the matrix. It suggests that adding NH_4Cl to the FAB matrix would be more helpful in enhancing the pseudo-molecular ion peak of saccharide compounds. This is consistent with the fact that

TABLE 2
The relative abundance of $[M+H]^+$ and $[M+NH_4]^+$ of compounds 17-24

Compound	$[M+H]^+$(%)	$[M+NH_4]^+$ (%)
17	181(<2) 165(<1)	198(30), 182(50)
18	181(<3) 165(<2)	198(38), 182(52)
19	181(<2) 151(<2)	198(56), 168(24)
20	181(<2) 343(<1)	198(63), 360(18)
21	165(<1), 343(<2)	182(45), 360(15)
22	181(<2), 151(<1), 165(<2)	198(42), 168(32), 182(38)
23	181(<2), 151(<1), 343(<1)	198(45), 182(33), 360(12)
24	165(<2), 181(<2), 343(<2)	182(37), 198(39), 360(10)

ammonium is likely to have better affinity with saccharide and form the complex $M\cdots NH_4^+$ between the cation and ligand (mono- or di- saccharide) in matrix solution, the peak heights of $[M+NH_4]^+$ have connection with the stability[2].

The abundance of $[M+H]^+$, and $[M+NH_4]^+$ of samples 18-24 is presented in Table 2. From the FAB data, it can also be seen that there is a strong $[M+NH_4]^+$ peak corresponding to each saccharide in the mixtures, whose abundance is much higher than that of $[M+H]^+$ peak, For example, in the FAB spectrum of sample 17 (which consists of glucose and rhamnose), with addition of NH_4^+ to the matrix, there are two strong peaks of the $[M+NH_4]^+$ ion (m/z at 198 and m/z at 165) besides two weak peaks of the $[M+H]^+$ ions (m/z at 181 and m/z at 151). This phenomenon may be used directly to determine the molecular weight of each saccharide in the mixtures.

It should be noted that the complex $[M+NH_4]^+$ is also formed between cation and the matrix at the same time that the NH_4^+ is mixed with the FAB matrix.. It is necessary to consider the contribution of the matrix, when determining the molecular weights of samples according to the adduct ion $[M+NH_4]^+$.

CONCLUSION

Formation of the complex $M \cdots NH_4^+$ between cation and ligand (mono- and di-saccharide) results in a dramatic pseudo-molecular ion of $[M+NH_4]^+$ with addition of an appropriate amount of NH_4Cl to the matrix. This makes it quite easy to determine the molecular weight of mono- and di-saccharide, and each component in the saccharide mixtures.

ACKNOWLEDGEMENTS

This project was supported by National Science Foundation of China and Chinese Postdoctoral Science Foundation.

REFERENCES

1. A. Dell, Adv. Carbohydr. Chem. Biochem., 45(1987), 20.
2. L. Fenselau and R. J. Cotter, Chem. Rev., 87(1987), 5011.
3. Mitsuo Takayama, Toshio Fukai and Taro Nomura, Org. Mass Spectrom., 26(1991), 655.
4. F. Z. Zhao, H. Q. Li, J. J. Zhai, N. Y. Chen and Y. Z. Chen, Acta Chimica Sinica. , 49(1991), 1487.
5. J. J. Zhai, F. Z. Zhao, H. Q. Li, N. Y. Chen and Y. Z. Chen, Acta Pharma Sinica., 27(1992), 434.
6. F. Z. Zhao, J. J. Zhai, H. Q. Li, N. Y. Chen and Y. Z. Chen, Acta Chimica Sinica., 51(1993), 173.
7. C. Bosso, A. Heyraud and L. Patron, Org. Mass Spectrom., 26(1991), 321.
8. F. W. Rollgen, U. Giessmann, F. Borchers and K. Levsen, Org. Mass Spectrom., 13(1978), 459.

Date Received: February 15, 1999
Date Accepted: March 1, 2000