OMS Letters

Dear Sir

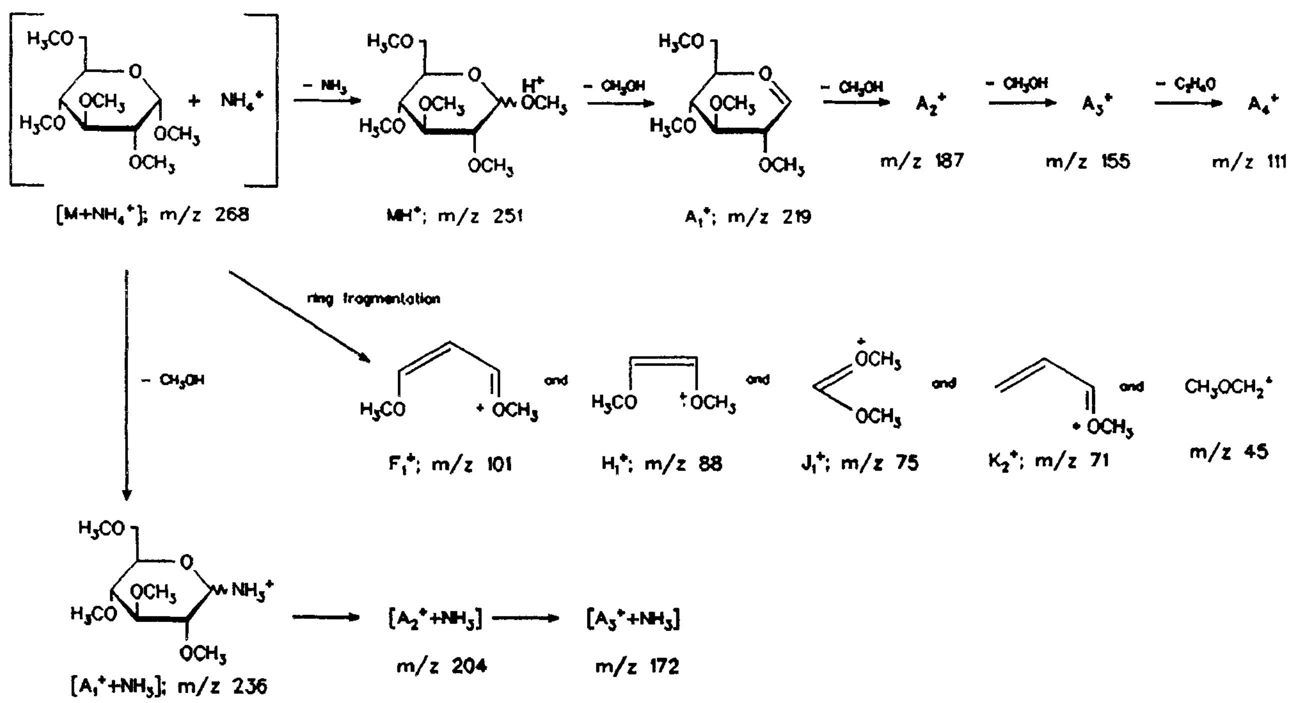
Mass-analysed Ion Kinetic Energy Spectra and Collisional Activation Spectra of Cluster Ions of Methyl 2,3,4,6-tetra-*O*-methyl-D-hexopyranosides with Ammonia and Methylamine

Per-*O*-methylated saccharides (M) react with protonated ammonia and protonated amines (RH^+), respectively, under the conditions of chemical ionization mainly by the formation of cluster ions $[M + RH^+]$.[1] In addition, cluster ions consisting of fragment ions formed by loss of the glycosidic group (so called type A^+ ions[2]) and the base R are observed. A Fourier-transform ion cyclotron resonance (FT-ICR) study has shown[3] that these latter cluster ions are also formed by a reaction of ions A^+ with NH_3. In the case of ions $A_1{}^+$ formed from methyl 2,3,4,6-tetra-*O*-methyl-D-hexopyranosides by loss of the glycosidic CH_3O group the rate for the formation of the adduct ions $[A_1{}^+ + NH_3]$ is rather small, but depends on the stereochemistry of the monosaccharide. Additional information about the structure and reactivity of both types of cluster ions can be gained by mass-analysed ion kinetic energy (MIKE) spectra and collisional activation (CA) spectra. In this letter, the results of a corresponding study of the $[M + RH^+]$ and $[A_1{}^+ + R]$ ($R = (NH_3$, $CH_3NH_2)$ of stereoisomeric per-*O*-methylated-D-hexopyranosides are discussed.

Methyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (**1**), methyl 2,3,4,6-tetra-*O*-methyl-β-D-galactopyranoside (**2**), and methyl 2,3,4,6-tetra-*O*-methyl-D-mannopyranoside (**3**) were used as model compounds. **1**–**3** were introduced into a modified chemical ionization (CI) ion source of a VG ZAB-2F mass spectrometer by a heated direct inlet system with a leak valve until the pressure reading at the ion gauge of the ion-source housing was 10^{-6}–10^{-5} mbar. Then, the reagent gas (NH_3 or CH_3NH_2) was introduced by the usual CI-gas inlet line until a sufficient intensity of the adduct ions was obtained, using 70 eV electron impact ionization and an ion-source temperature of about 190 °C. The ions under study were focused magnetically into the 2nd field-free region of ZAB-2F mass spectrometer, and the MIKE and CA spectra were obtained by scanning the voltage of the electrostatic analyser. Helium gas was used for collision-induced dissociation in the collision cell of the 2nd field-free region.

The MIKE spectra of the cluster ions $[M + NH_4{}^+]$ exhibit only a peak for the loss of NH_3. The cluster ions $[M + CH_3NH_3{}^+]$ appear to be even more stable and show no distinct peaks of fragment ions in their MIKE spectra. However, for both types of cluster ions collisional activation brings about extensive fragmentations. The CA spectra thus obtained from the cluster ions derived from the methyl 2,3,4,6-tetra-*O*-methyl-D-hexopyranosides (**1**–**3**) are presented in Tables 1 and 2. The fragmentation follows several pathways which are depicted in Scheme 1 for the $[M + NH_4{}^+]$ ions from **1**. The main fragmentation routes of $[M + NH_4{}^+]$ and $[M + CH_3NH_3{}^+]$ start by loss of NH_3 and CH_3NH_2, respectively, yielding MH^+ ions at *m/z* 251, and continues by subsequent eliminations of methanol and eventually a fragment of 44 Dalton yielding the ions A_1(*m/z* 219), A_2(*m/z* 187), A_3(*m/z* 155) and A_4(*m/z* 111). This series of eliminations is expected from the fragmentations of **1**–**3** under CI conditions.[4] In the case of the cluster ions $[M + NH_4{}^+]$ another series of collision-induced eliminations arises from subsequent losses of methanol directly from the cluster ion yielding ions $[A_1{}^+ + NH_3]$(*m/z* 236), $[A_2{}^+ + NH_3]$(*m/z* 204) and $[A_3{}^+ + NH_3]$(*m/z* 172). The ions $[A_1{}^+ + NH_3]$(*m/z* 236) are identical to those formed by an ion–molecule reaction between ions $A_1{}^+$ and NH_3 in the FT-ICR spectrometer.[3] The relative abundances of this series of ions is quite small. Nevertheless, their formation is of interest since it indicates probably a covalent bonding of the NH_3 group in some of the cluster ions. An analogous series of ions it not, however, observed in the CA spectra of the cluster ions $[M + CH_3NH_3{}^+]$.

Another observation is the formation of abundant fragment ions $F_1{}^+$(*m/z* 101), $H_1{}^+$(*m/z* 88), $J_1{}^+$(*m/z* 75) and $K_1{}^+$ (*m/z* 71), by collisional activation of both types of cluster ions.



Scheme 1. Fragmentation of $[M + NH_4]^+$ from **1** (D-gluco).

0030-493X/91/090809-02 $05.00

Received 28 June 1991
Accepted 29 June 1991

Table 1. CA mass spectra of ions [M + NH_4^+](*m/z* 268) of methyl 2,3,4,6-tetra-*O*-methyl-D-hexopyranosides (1–3)

m/z	Ion structure	1 (D-gluco)	2 (D-galacto)	3 (D-manno)
251	[M + H^+]	34	100	43
236	[A_1^+ + NH_3]	3	2	3
219	A_1^+	76	67	100
204	[A_2^+ + NH_3]	1	1	1
187	A_2^+	100	48	36
172	[A_3^+ + NH_3]	1	1	1
155	A_3^+	9	2	3
145		5	2	3
111	A_4^+	34	23	13
101	F_1^+	70	39	55
88	H_1^+	29	14	23
75	J_1^+	24	9	16
71	K_2^+	25	8	15
45	$CH_3OCH_2^+$	30	13	18

Table 2. CA mass spectra of ions [M + $CH_3NH_3^+$] (*m/z* 282) of methyl 2,3,4,6-tetra-*O*-methyl-D-hexopyranosides (1–3)[a]

m/z	Ion structure	1 (D-gluco)	2 (D-galacto)	3 (D-manno)
251	[M + H^+]	10	3	8
219	A_1^+	30	100	100
187	A_2^+	73	90	80
155	A_3^+	10	10	12
127		15	10	13
111	A_4^+	30	40	45
101	F_1^+	100	90	85
88	H_1^+	51	40	43
75	J_1^+	37	20	28
71	K_2^+	30	15	22
45	$CH_3OCH_2^+$	30	28	28
32	$CH_3NH_3^+$	302	180	290

[a] The $CH_3NH_3^+$ ion, *m/z* 32, was not selected as the base peak.

Table 3. CA mass spectra of the ions [A_1^+ + NH_3](*m/z* 236) from methyl 2,3,4,6-tetra-*O*-methyl-D-hexopyranosides (1–3)

m/z	Ion	1	2	3	*m/z*	Ion	1	2	3
219	A_1^+	38	100	100	111	A_4^+	29	25	27
204	A_2^+ + NH_3	13	20	5	101	F_1^+	56	45	66
187	A_2^+	100	95	56	88	H_1^+	44	50	19
172	A_3^+ + NH_3	2	2	4	75	J_1^+	24	20	16
155	A_3^+	7	14	10	71	K_2^+	26	15	25
143		12	21	15	45	$CH_3OCH_2^+$	26	26	39

These fragment ions have to arise from cleavages of the pyranose ring of the cluster ions, and they are considered usually as typical of the electron-impact induced fragmentation of the molecular ions of *O*-methylated sugars,[2,5] initiated by a cleavage of the pyranose ring. Their abundant formation from the cluster ions may possibly be an indication that the pyranose ring has already been cleaved during the formation of the cluster ions.

The collision-induced decompositions of the ions [A_1^+ + NH_3] were also studied (Table 3). Again the spectra show intense peaks of the ring-cleavage fragment ions F_1^+, H_1^+, J_1^+ and K_2^+, besides the series of ions A^+ arising from subsequent losses of methanol. This finding supports the assumption that the cluster ions [A_1^+ + NH_3] also contain at least some contribution of ions with an open-chain structure besides the usually proposed ring structure.

Finally, it should be noted that a comparison of the CA spectra of the cluster ions [M + NH_4^+], M = **1**, **2**, **3**, (Table 1) reveals remarkable differences of the relative intensities of characteristic ions, in particular of the *A* ions *m/z* 251, *m/z* 219 and *m/z* 187. Similar but less pronounced intensity differences are observed in the CA spectra of the cluster ions [M + $CH_3NH_3^+$] from the stereoisomeric monosaccharide **1–3** (Table 2). Since the cluster ions [M + NH_4^+] give rise to very large peaks in the CI(NH_3) mass spectra and can be measured conveniently by CA mass spectrometry, this dependence of the CA spectra on the stereochemistry of the sugar can be used with some benefit for the mass spectral analysis of *O*-methylated saccharides.

Yours

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References

1. V. Kováčik and H.-Fr. Grützmacher, *Org. Mass Spectrom.* **25**, 687 (1990).
2. N. K. Kochetkov and O. S. Chizhov, *Adv. Carbohydr. Chem.* **21**, 39 (1966).
3. V. Kováčik, J. Hirsch, D. Thölmann and H.-Fr. Grützmacher, *Org. Mass Spectrom.*, to be published.
4. (a) A. M. Hogg and T. L. Nagabhushan, *Tetrahedron Lett.* 4827 (1972); (b) D. Horton, J. D. Wander and R. Foltz, *Carbohydr. Res.* **36**, 75 (1974).
5. K. Heyns, H.-Fr. Grützmacher, H. Scharmann and D. Müller, *Fortschr. Chem. Forsch.* **13**, 448 (1966).