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-glucopyranosides 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⁺]. In addition, cluster ions consisting of fragment ions formed by loss of the glycosidic group (so-called type A⁺ ions) and the base R are observed. A Fourier-transform ion cyclotron resonance (FT-ICR) study has shown that these latter cluster ions are also formed by a reaction of ions A⁺ with NH₃. In the case of ions A⁺ formed from methyl 2,3,4,6-tetra-O-methyl-D-glucopyranosides by loss of the glycosidic CH₃O group the rate for the formation of the adduct ions [A⁺ + NH₃] is rather small, but depends on the stereocchemistry 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 + NH₃⁺] and [A⁺ + R] (R = NH₃, CH₃NH₂) of stereoisomeric per-O-methylated-D-glucopyranosides are discussed.

Methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside (1), methyl 2,3,4,6-tetra-O-methyl-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 (NH₃, CH₃NH₂) was used for collision-induced dissociation in the collision cell 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 + NH₃⁺] exhibit only a peak for the loss of NH₃. The cluster ions [M + CH₃NH₂⁺] 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-glucopyranosides (1–3) are presented in Tables 1 and 2. The fragmentation follows several pathways which are depicted in Scheme 1 for the [M + NH₃⁺] ions from 1. The main fragmentation routes of [M + NH₃⁺] and [M + CH₃NH₂⁺] start by loss of NH₃ and CH₃NH₂, 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 A₁(m/z 219), A₂(m/z 187), A₃(m/z 155) and A₄(m/z 111). This series of eliminations is expected from the fragmentations of 1–3 under CI conditions. In the case of the cluster ions [M + NH₃⁺] another series of collision-induced eliminations arises from subsequent losses of methanol directly from the cluster ion yielding ions A₁⁺ + NH₃(m/z 236), A₂⁺ + NH₃(m/z 204) and A₃⁺ + NH₃(m/z 172). The ions [A₁⁺ + NH₃](m/z 236) are identical to those formed by an ion-molecule reaction between ions A₁⁺ and NH₃ in the FT-ICR spectrometer. 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 NH₃ 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 + CH₃NH₂⁺].

Another observation is the formation of abundant fragment ions F₁⁺(m/z 101), H₁⁺(m/z 88), J₁⁺(m/z 75) and K₁⁺(m/z 71), by collisional activation of both types of cluster ions.

Scheme 1. Fragmentation of [M + NH₃⁺] from 1 (D-gluco).

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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,\(^*\) 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 \([A_1^+ + \text{NH}_3]\) were also studied (Table 3). Again the spectra show intense peaks of the ring-cleavage fragment ions \(F_1^+, H_1^+, J_1^+,\) and \(K_1^+,\) besides the series of ions \(A^+\) arising from subsequent losses of methanol. This finding supports the assumption that the cluster ions \([A_1^+ + \text{NH}_3]\) 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 \([M + \text{NH}_4^+]\), \(M = 1, 2, 3,\) (Table 1) reveals remarkable differences of the relative intensities of characteristic ions, in particular of the \(A^+\) ions, in \(m/z\) 251, \(m/z\) 219, and \(m/z\) 187. Similar but less pronounced intensity differences are observed in the CA spectra of the cluster ions \([M + \text{CH}_3\text{NH}_2^+]\) from the stereoisomeric monosaccharides 1–3 (Table 2). Since the cluster ions \([M + \text{CH}_3\text{NH}_2^+]\) give rise to very large peaks in the \(\text{Cl(NH}_3^+\) 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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