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Low-energy collisionally activated dissociation of pentose–borate complexes

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ABSTRACT

Pentose–borate 1:1 complexes were generated in the ESI source of a triple quadrupole and ion trap mass spectrometer by electrospray ionization of $Na_2B_4O_7$ and pentose (arabinose, lyxose, ribose, xylose) 2:1 solution in CH_3CN/H_2O. The study of their low-energy collisionally activated dissociation (CAD) demonstrated that ribose and lyxose are preferentially complexed at the C_2–C_3 *cis*-diol function whereas arabinose and xylose are esterified at the C_1–C_2 hydroxyl groups. No evidence was found of the stronger affinity for ribose to borate. The ribose probiotic rule can be explained by considering its peculiar capability, among the investigated pentoses, to almost totally complex the borate anion at the C_2–C_3 hydroxyl group, thus enabling the subsequent stages of nucleotide assembly, such as phosphorylation and linkage to the nucleobases.

Finally, the differences observed in the pentose–borate complex CAD spectra can be used for the mass spectrometric discrimination of isomeric pentoses in complex mixtures.

1. Introduction

The complexation of borate ions with carbohydrates in solution has been known for a long time. In 1949 Deutsch first demonstrated that boric acid can easily form 1:1 and 1:2 complexes with the C_2–C_3 and C_4-C_5 *cis*-diols of mannitol [1]. The stereospecific addition of borate ions to vicinal hydroxyl groups had been widely used for the identification and structural discrimination of several saccharides. The formation of stable borate complexes with ribose suggested a fascinating hypothesis concerning boron evolvement in the evolution of a ribonucleic acid (RNA) world. Indeed, it has been demonstrated that borate minerals play an important role in the spontaneous biosynthesis of pentoses from simple organic precursors. By stabilizing the formation of diol precursors and preventing their degradation, borate minerals probably promote a ribose nucleic world in preference to the other pentoses [2].

Verchere used ^{11}B and ^{13}C NMR spectroscopy to first report that pentoses are complexed by boric acid in the furanose form [3,4]. Arabinose and xylose give rise to the same type of complex involving the anomeric hydroxyl group whereas ribose and lyxose may form two different species as borate is bound either at C_1–C_2 or at C_2–C_3 *cis*-diols. As a result, chelate formation between arabinose and xylose sugars with boric acid is not as easy as between ribose and lyxose. In view of these interesting results, a survey of studies addressing the structure of borate–carbohydrate complexes has been made. The formation of pyranose boronate esters has been hypothesized by some groups whereas others have confirmed the furanose complexation reported by Verchere. Assuming pentose complexation in the furanose form, the question of whether the borate–pentose complexes have a bi- or tridentate coordination and whether ribose is preferentially complexed at the C_1–C_2 or C_2–C_3 *cis*-diol groups is still an open one. For the sake of example, two recent NMR studies in alkaline aqueous medium indicate a C_1–C_2–C_3 tridentate structure and a C_1–C_2 bidentate one, respectively [5,6], for the ribose–boronate ester.

The fragmentation of monosaccharides, and not only pentoses, were widely studied using mass spectrometry as a tool to distinguish between isomeric species. Field desorption ionization of selected monosaccharide isomers by Deutsch [1] shows that furanoidal ketoses tend to lose a methanol molecule whereas pyranoidal aldose fragmentation is characterized by water elimination. Pyranose and furanose structures of pentoses and hexoses can be efficiently distinguished in electrospray mass spectrometry by generating and subsequently fragmenting the corresponding cationized ions [7,8]. Interesting stereochemical assignment of hexose and pentose isomeric residues in flavonoid O-glycosides is possible using CAD mass spectrometry [9]. The chemical ionization of mono- and disaccharides using trimethyl borate as reagent gas first reproduced in the gas phase the known specific stereochemical reaction of the borate ions with *cis*-diols in solution [10]. The capability of toluneboronic acid to form interesting esters whose intensity depends on hydroxyl orientation provides useful information about polyhydroxy compound

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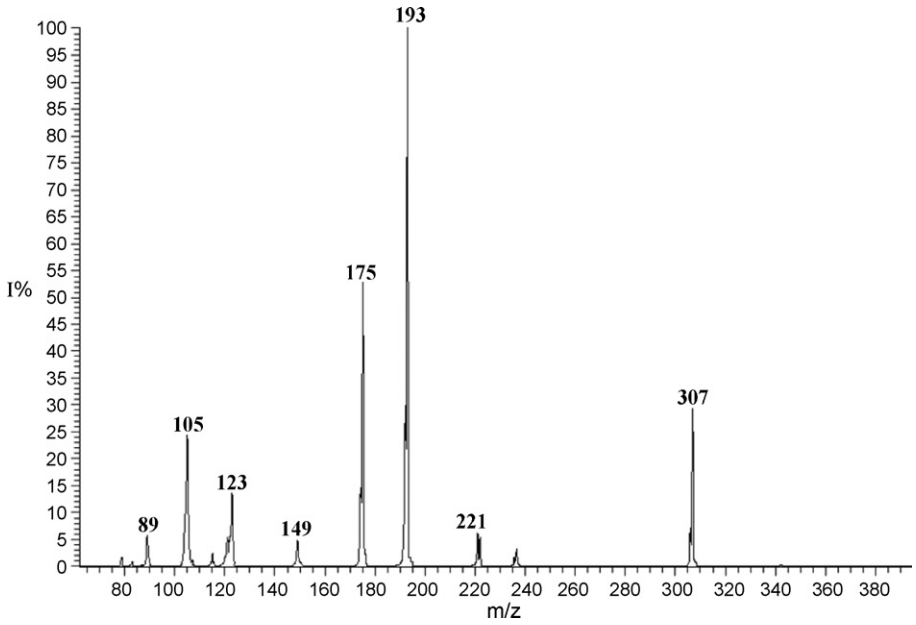


Fig. 1. Ion trap ESI spectrum of $Na_2B_4O_7$ and ribose (2:1) solution in CH_3CN/H_2O (3:1).

stereochemistry although the authors assumed the sugars had a pyranose structure [11–13]. Thermospray mass spectrometric studies in positive ion mode confirmed the borate's ability to generate furanosic complexes having a higher stability in the case of ribose and lyxose isomers than arabinose and xylose, indicating that borate complexation occurs preferentially across the 1,2 OH groups [14]. Sugar alcohol discrimination throughout borate complexation was demonstrated in plant extracts by the MALDI/FTMS technique [15]. The ESI-CID of several 1,2 *cis*-diol-boric acid complexes, including mannitol and sorbitol, led Terlouw and coworkers to describe peculiar structurally informative fragmentation and highlight how 1,3 and 1,4-diols do not form stable acid boric complexes [16]. The joint application of ESI mass spectrometry and ^{11}B NMR spectroscopy allowed borate esterification to be studied with biologically active compounds such as NAD and NADH [17]. Continuing the study about borate involvement in the ribonucleic acid biosynthesis, Powell et al. compared pentose isomers intensity with an internal standard using DIOS mass spectrometry. They determined pentose preferential order of binding to boron as ribose > lyxose > arabinose > xylose by the relative ion intensities [18]. The structure and the stability order of 2:1 pentose–borate complexes were also predicted by theoretical calculations. The computed stability order was ribose > xylose > lyxose > arabinose and the O_1, O_2 binding was found to be energetically more favorable than O_2, O_3 [19].

Recently the interactions of the most abundant anions in seawater (borate, sulfate and carbonate) with D-ribose were studied by ^{1}H, ^{11}B and ^{13}C NMR spectroscopy [4]. The authors confirmed that only borate improves the stability of D-ribose which is preferentially complexed in the C_1–C_2 position.

The present study was carried out for the specific purpose of investigating the structure of 1:1 borate–pentose (ribose, lyxose, arabinose, xylose) complexes by triple quadrupole and ion trap CAD mass spectrometry in order to demonstrate the preferred site of complexation of the different pentoses, the possibility of their discrimination and to prove the hypothesized highest affinity of ribose for the borate ions. The results shed new light on the nature of borate complexation with pentoses in the gas phase and demonstrate the possibility of discriminating pentoses by low-energy CAD mass spectrometry.

2. Materials and methods

2.1. Materials

D-Lyxose, D-arabinose, D-ribose, D-ribonic-γ-lactone, 1,4-anhydroerythritol, D-glucurono-6-3-lactone and sodium tetraborate decahydrate were purchased from Sigma–Aldrich Co. with a stated purity of 99.99 mol%. D-Xylose was purchased from Merck.

2.2. Mass spectrometric experiments

Triple quadrupole mass spectrometric experiments were performed with a TSQ700 instrument from Thermofinnigan Ltd. The ions were generated by negative electrospray ionization of a 3×10^{-4} M $Na_2B_4O_7$ and pentose (arabinose, lyxose, ribose, xylose) 2:1 solution in CH_3CN/H_2O (3:1) directly infused by a syringe pump at a flow of 20 μl/min. The solutions were prepared by diluting 40–50 μl of a master borate/pentose 2:1 solution at a total concentration of 4×10^{-2} M with 6 ml of CH_3CN/H_2O (3:1) Typical operating conditions were: needle voltage 3.0 kV, flow rate 20 μl min^{-1}, capillary temperature 150 °C, capillary exit and skimmer voltage 80 and 120 V, respectively, hexapole dc offset 2 V.

The ions generated in the ESI source were driven into the collision cell, actually a RF-only hexapole, containing the neutral reagent. The collisionally activated dissociation (CAD) spectra were recorded using Ar as the target gas at pressures of about 0.1 mTorr and at collision energies ranging from 0 to 30 eV (laboratory frame). An upper limit of 2–3 eV for the kinetic energy of the reactant ion at nominal collision energy of 0 eV (laboratory frame) and an ion beam energy spread of about 1 eV was estimated by using cut-off potentials. The charged fragments were analyzed with the third quadrupole, scanned at a frequency of 150 Da s^{-1}.

The ion trap spectra were recorded with an LCQ quadrupole ion trap mass spectrometer (Thermo-Quest, Finnigan, San José, CA, USA) equipped with an electrospray ionization source. In the negative ion mode the spray voltage was set to 3.8 kV and the capillary voltage to −100 V. The tube lens offset and all other parameters were optimised for maximum transfer of ions to the ion trap. The capillary temperature was set at 150 °C and the sample injection flow rate was 10 μl/min. Mass spectra were recorded by scanning

the mass analyzer from m/z 100 to m/z 1000 with 6 total microscans. Maximum injection time into the ion trap was 500 ms.

3. Results

Pentose–borate ions $[C_5H_{10}O_7B]^-$ are generated in the source of the triple quadrupole and ion trap mass spectrometers by electrospray ionization of $Na_2B_4O_7$ and pentose (arabinose, lyxose, ribose, xylose) 2:1 solution in CH_3CN/H_2O (3:1). The ESI full spectra display the mono-pentose–borate complex at m/z 193 as the major peak (Fig. 1). Higher absolute intensities of this species are observed in ribose and lyxose solutions than in arabinose and xylose.

The borate excess is a critical feature in the generation of the 1:1 pentose–borate complexes since a different ratio obtained by increasing the sugar amount dramatically enhances the formation of the 1:2 complexes at m/z 307.

The ion at m/z 175 derives from the mono-pentose–borate complex through the loss of a water molecule whereas the ionic species at m/z 123, m/z 105 and m/z 89 are characteristic of the ESI spectra of borate solutions and their intensity increases as the solution ages or as it becomes too concentrated.

Therefore, the solutions are daily prepared at a concentration of approximately 4×10^{-5} M.

3.1. Structural characterization of the pentose–borate complexes

Collisionally activated dissociation (CAD) mass spectrometry was used to investigate the structure of the pentose–borate complexes.

3.1.1. Triple quadrupole (TQ) experiments

The CAD spectra of the pentose–borate complexes at m/z 193 performed in the TQ mass spectrometer at a nominal collision energy of 25 eV (laboratory frame) are reported in Fig. 2. The loss of two water molecules leads to the ions at m/z 175 and m/z 157. The first water molecule is presumably lost from the borate moiety whereas the second one necessarily involves one of the sugar hydroxyl groups.

Following the loss of the first water molecule (see below), the formation of the fragment at m/z 115 is observed. By comparing the intensity of this species with that of the ion at m/z 157 it is evident that their ratio is practically maintained in all the CAD spectra of the different sugar complexes. This fragmentation is a common pentose dissociation channel that involves the cleavage of the sugar ring between the bonds O–C_1 and C_3–C_4 leading to the elimination of 60 Da [20].

Conversely, it is interesting to note the specific relative intensity of the fragment ions at m/z 113 and m/z 103 observed for each pentose–borate complex. The ion at m/z 113 is generated by the loss of a H_3BO_3 molecule whereas the lesser fragmentation into the ion at m/z 103 is due to the loss of 90 Da involving the cleavage of the sugar ring between the bonds O–C_1 and C_2–C_3.

The relative intensities of these two dissociation channels are higher in the xylose and arabinose–borate complexes than in ribose and lyxose. In particular a characteristic and reproducible ratio between the ions at m/z 115 and m/z 113 may be observed in the CAD spectrum of each pentose–borate anion, and is found to be 8.8 for ribose, 5.5 for lyxose, 2.5 for arabinose and 0.9 for xylose.

The mass attribution of the fragments still containing the boron atom was confirmed by the shift of one m/z unit observed in the CAD spectrum of the corresponding $[C_5H_{10}O_7{}^{10}B]^-$ ions. According to the mass attribution, the ion at m/z 113 is the only ionic fragment that does not shift in the $[C_5H_{10}O_7{}^{10}B]^-$ CAD spectrum.

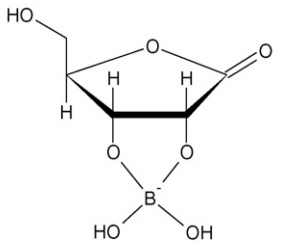
The TQ energy resolved CAD spectra of the $[C_5H_{10}O_7B]^-$ ions recorded at collision energies ranging from 0 to 25 eV (laboratory frame) allow the relative dissociation energies of the observed fragmentation channels to be investigated. Interestingly, similar threshold energies among the different sugar–borate complexes were measured for all the observed dissociations. In Figs. 3 and 4 the profiles of the relative intensities of the fragments at m/z 175 (loss of H_2O) and m/z 113 (loss of H_3BO_3) are reported as a function of the increasing collision energy.

The loss of the first water molecule from the borate moiety is characterized by a comparable absolute intensity for all the pentose–borate complexes investigated. Conversely, the loss of H_3BO_3 is characterized by a lower intensity in the case of ribose (magnified six times) and lyxose (magnified five times) than arabinose and xylose.

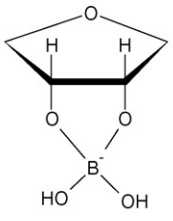
3.1.2. Ion trap experiments

The sequences of the fragmentation channel observed in the TQ experiments were clarified by MS^n experiments performed by the ion trap mass spectrometer. According to the TQ results, the easy loss of a water molecule was observed after the isolation of each mono-pentose–borate complex at m/z 193. The MS^3 of the fragment ion at m/z 175 shows the loss of an additional water molecule, the cleavage of the sugar ring and the loss of the boric acid leading to the ions at m/z 157, m/z 115 and m/z 113, respectively (Fig. 5). Xylose- and arabinose–borate complex MS^3 CAD spectra are characterized by the presence of higher intensities of the fragment at m/z 113 that practically disappear in the ribose spectra, which are conversely characterized by a higher intensity of the ion at m/z 115 due to the cleavage of the sugar ring. The value of the ratio between the ion at m/z 115 and m/z 113 measured in the ion trap CAD spectra is slightly different and less reproducible than that observed in the TQ experiments, while nevertheless remaining specific for each pentose–borate complex investigated.

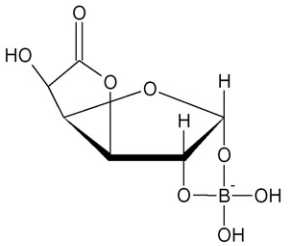
In order to obtain additional structural information about the borate–pentose complexation the collisionally activated dissociations of model compounds were investigated. The model compound taken into account for the comparison were ribonic-γ-lactone, 1,4-anhydroerythritol and D-glucurono-6-3-lactone. The borate complexation of these species leads to the following model structures:



Ribonic-γ-lactone-borate ester



1,4-anhydroerythritol-borate ester



D-glucurono-6-3-lactone-borate ester

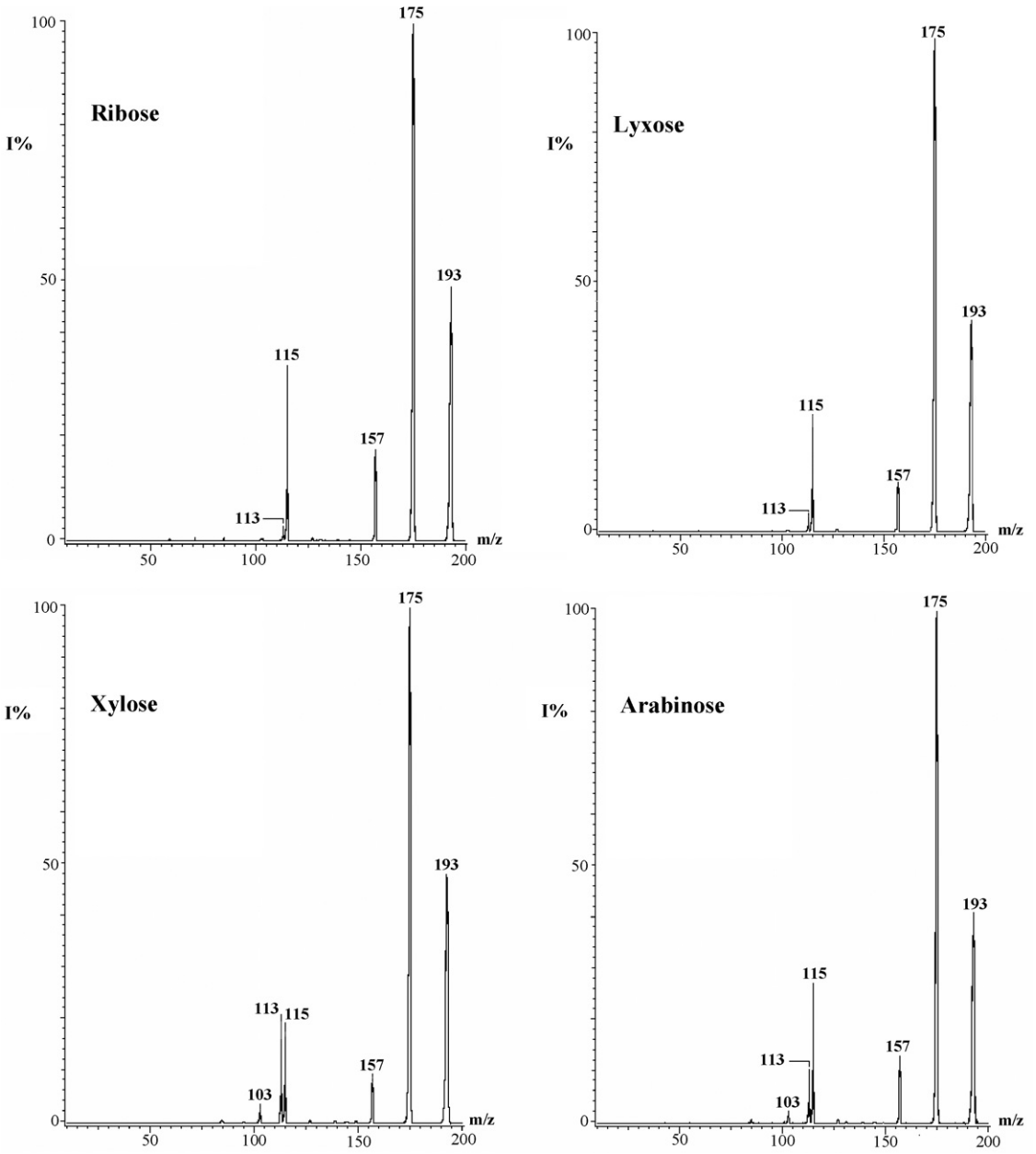


Fig. 2. Triple quadrupole CAD mass spectra of the pentose–borate complexes.

Ribonic-γ-lactone and 1,4-anhydroerythritol have a simple furanosic structure characterized by the presence of the *cis*-diol function which is able to bind the borate moiety in the C_2–C_3 position whereas D-glucurono-6-3-lactone is characterized by the available *cis*-diol group in the C_1–C_2 position. The only CAD fragmentation of 1,4-anhydroerythritol, D-glucurono-6-3-lactone and ribonic-γ-lactone–borate complexes is the loss of a water molecule leading to the fragment ions at *m*/*z* 129, *m*/*z* 173 and *m*/*z* 201, respectively. By isolating these ionic species solely the dissociation of the furanosic ring is observed.

4. Discussion

The well-known ability of borate to form complexes with vicinal *cis*-diols or proximal hydroxyl in correct orientation makes it possible to hypothesize the structure of each pentose–borate complex. Several studies have demonstrated that pentoses are complexed in the furanosic form rather than in the pyranose form while the possible formation of bidentate or tridentate structures is still controversial. In particular for the ribose–borate complex a 1,2,3 tridentate structure was recently proposed as the sole species present in solution whereas arabinose and xylose are characterized by a 1,2 bidentate complex together with a 1,2,5 and 1,3,5 tridentate structure, respectively. The gas phase 1:1 pentose–borate complex at *m*/*z* 193 initially formed in the ESI source is characterized by a bidentate structure whereas the ion at *m*/*z* 175 generated from the ion at *m*/*z* 193 by the loss of a water molecule may in principle present also the tridentate structure evidenced in solution.

Considering both α and β anomeric furanose cyclic structures for each aldopentose, the formation in the ESI mass spectrometric condition of the following bidentate and tridentate borate–pentose complexes can be hypothesized.

Although no data were reported concerning a possible 1,2,3 tridentate structure for the lyxose–borate complex we hypothesized its existence by analogy with ribose.

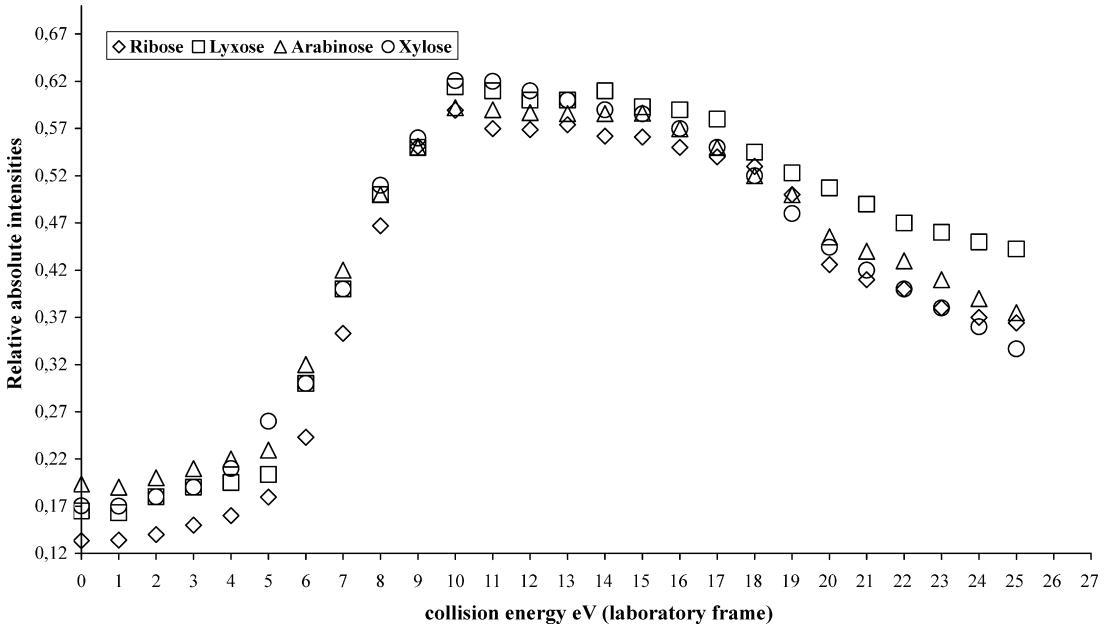


Fig. 3. Profiles of the ionic intensities of the fragment at *m*/*z* 175 as a function of the increasing collision energy.

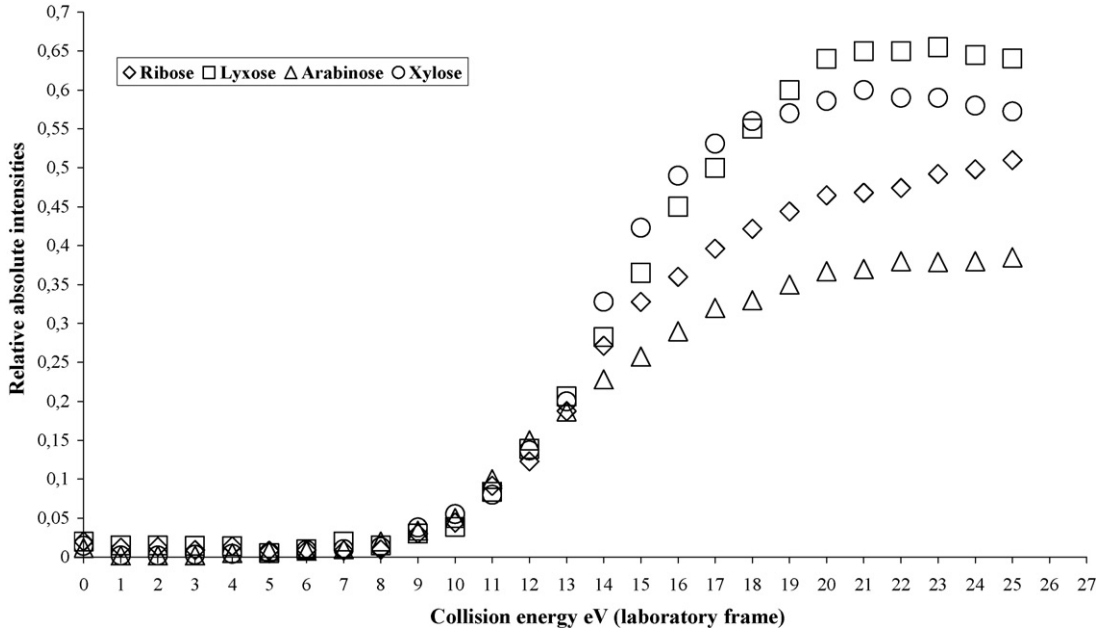
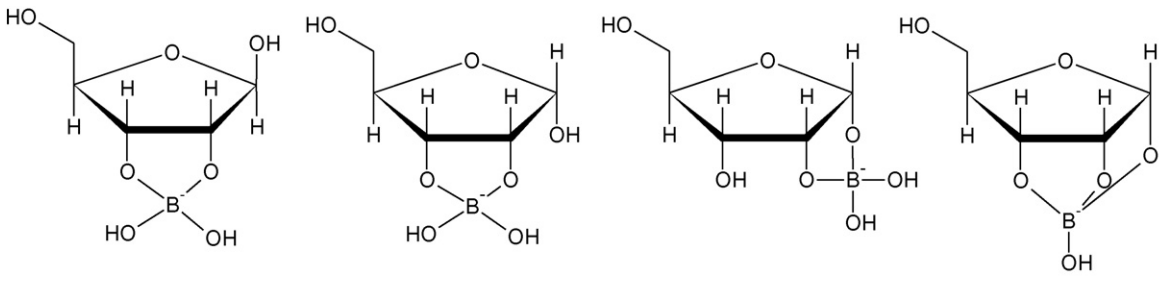


Fig. 4. Profiles of the ionic intensities of the fragment at *m*/*z* 113 as a function of the increasing collision energy.



β-ribose 2,3 borate ester α-ribose 2,3 borate ester α-ribose1,2 borate ester α-ribose1,2,3borate ester

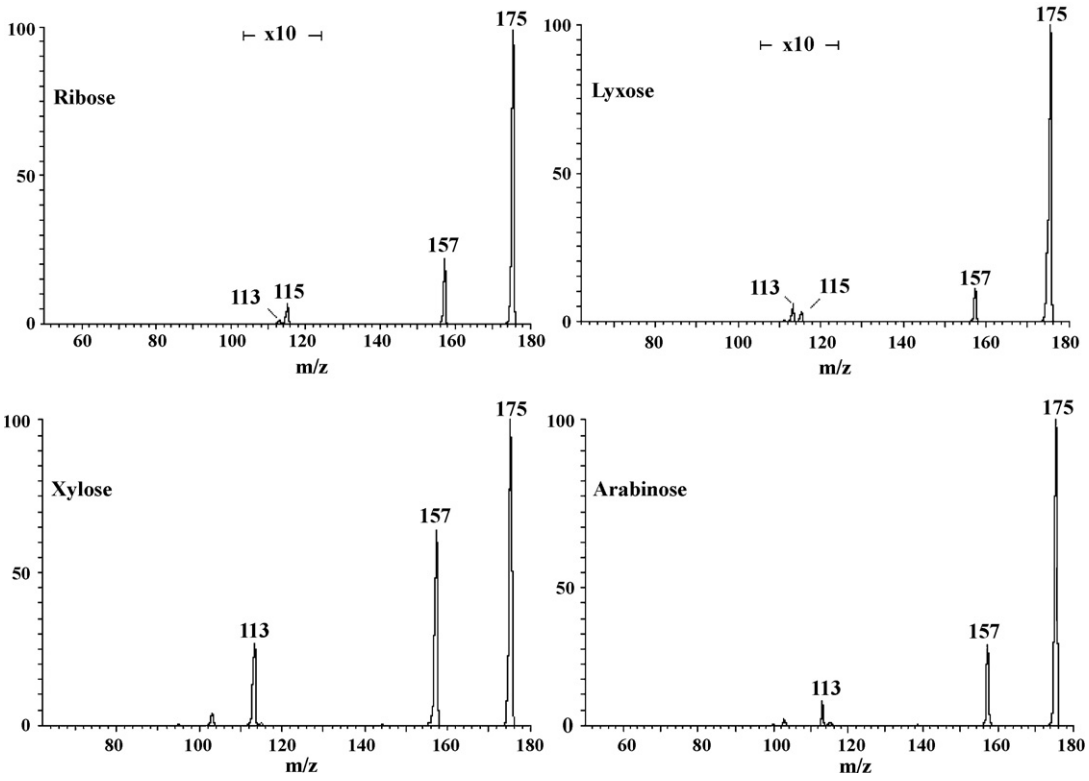
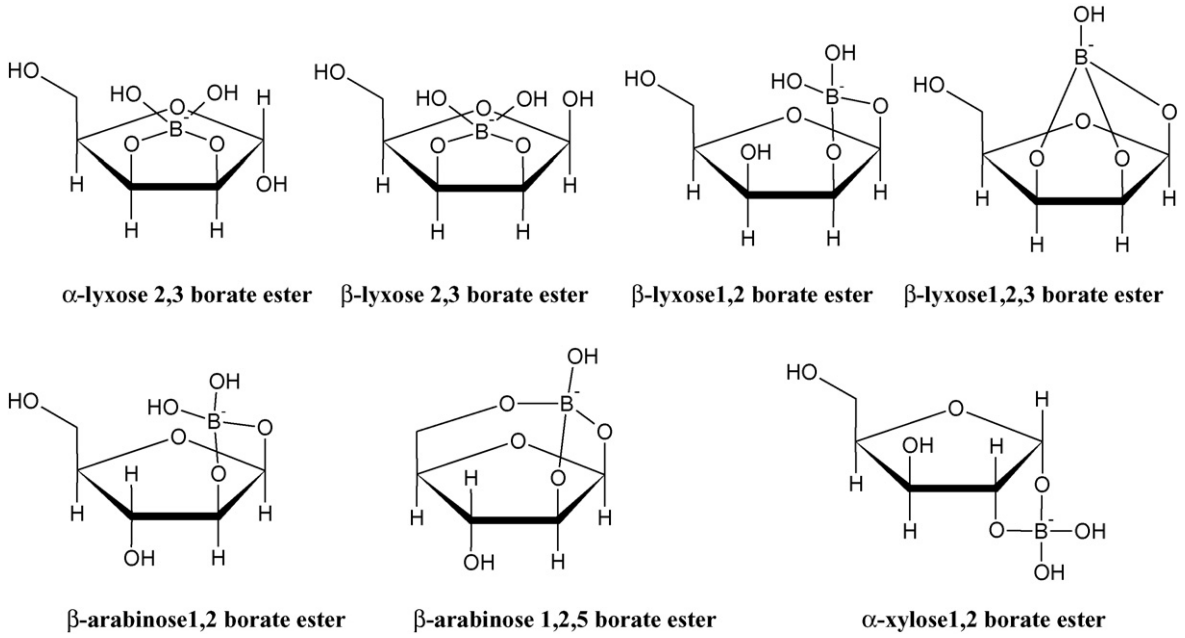


Fig. 5. Ion trap MS^3 spectra of the fragment at m/z 175.



The α and β ribose and lyxose anomers allow the formation of the borate complexes with both the available C_1–C_2 and C_2–C_3 *cis*-diol groups whereas β-arabinose and α-xylose may form the mono-pentose–borate complex by addition to the C_1–C_2 hydroxyl groups. Accordingly, the ESI spectra of borate–ribose and borate–lyxose solutions displayed a higher absolute intensity of the ion at m/z 193 than the corresponding solutions containing arabinose and xylose. Xylose is the only pentose whose initially formed borate complex cannot generate a tridentate structure and hence can be considered as a model ion of the C_1–C_2 *cis*-diol borate complexation.

Taking into account the CAD spectra of the model ion obtained by the addition of borate to 1,4-anhydroerythritol, ribonic-γ-lactone and D-glucurono-6-3-lactone, the loss of the first water molecule involves the borate moiety and is ascribable to borate addition at both the C_1–C_2 and C_2–C_3 *cis*-diols. As evidenced by the ribonic-γ-lactone–borate complex the C_5 hydroxyl group is not responsible for the loss of the second water molecule which, conversely, necessarily involves the C_1 or C_3 OH group not bound to the borate moiety.

The loss of the first water molecule leading to the ion at m/z 175 could be responsible for the formation of the different tridentate

structures hypothesized in solution for arabinose and ribose but its relative intensity and appearance energy are unaffected by the different pentoses involved. In addition, the comparable threshold energies measured for all the predominant dissociations of the different pentose–borate complexes demonstrate that these fragmentations involve the cleavage of the same bond and hence the formation of different tridentate structures seems to be excluded.

The ion trap CAD spectra demonstrate that the loss of H_3BO_3 is due to the dissociation of the daughter ion at *m*/*z* 175 and in particular is a characteristic dissociation of arabinose- and xylose–borate complexes whereas it has a very low intensity in the case of lyxose and ribose. This evidence clearly demonstrates that the loss of H_3BO_3 is specific to borate esterification at the C_1–C_2 *cis*-diol which represents the sole site of esterification of arabinose and xylose. The presence in the arabinose–borate complex TQ CAD spectrum of the fragment ions at *m*/*z* 115 and *m*/*z* 103, whose formation necessarily requires the C_5 hydroxyl group to be free, again allowed the formation in the gas phase of the C_1–C_2–C_5 tridentate structure reported in solution to be ruled out.

The addition of borate to ribose occurs preferentially at the C_2–C_3 position. The lower amount of complexation at the C_1–C_2 *cis*-diols is evidenced by the very low intensity of the fragment ion at *m*/*z* 113 although its appearance energy is comparable to the other pentose–borate complexes.

Lyxose complexation occurs at both C_1–C_2 and C_2–C_3 *cis*-diols and the increased intensity of the fragmentation into H_3BO_3 seems to indicate greater C_1–C_2 borate ester formation.

With regard to the binding preferences of borate to pentoses, the observed borate affinity order ribose > lyxose > arabinose > xylose probably reflects the different complexation sites present in the different sugars, taking into account their anomeric composition in solution. Ribose furanose isomers prefer the β anomeric structure with a β/α ratio of about 2 while the other pentoses have a higher abundance of the α form with a β/α ratio of 0.6 for arabinose, 0.35 for lyxose and 0.8 for xylose. From this point of view, also considering possible fast anomer interconversion, ribose and lyxose are characterized by having more conformations available that can generate borate complexes and so their esterification is highly facilitated compared with the other pentoses. Xylose was found to be the worst borate ligand since only its less abundant α anomer can be complexed. Furthermore, the fragmentation leading to the loss of H_3BO_3 peculiar to the borate addition to the C_1–C_2 *cis*-diols, is characterized by threshold energy comparable among the different pentose–borate complexes, as no evidence of ribose having a higher borate affinity was found in the ESI mass spectrometric condition used.

Conversely, the ribose probiotic rule can be explained by considering its capability to preferentially complex the borate at the C_2–C_3 hydroxyl groups. This would leave the C_1 and C_5 hydroxyl groups free to undergo the subsequent stages of nucleotide assembly, such as phosphorylation and linkage to the nucleobases.

As far as discrimination of the different pentose isomers by mass-spectrometric techniques is concerned, the differences observed in the CAD spectra can certainly be taken into account for their identification.

The specific ratio of the relative intensity of the fragment ions at *m*/*z* 113 and *m*/*z* 115 observed both in the TQ and ion trap CAD spectra, as well as the fragment ion at *m*/*z* 103, are characteristic features of each pentose–borate complex and could be useful for distinguishing them in complex mixtures.

5. Conclusions

The borate complexation of ribose, lyxose, arabinose and xylose in the furanose form was studied by low-energy CAD mass-spectrometric techniques. The comparison with the CAD spectra of model ion and the observation of the relative fragmentation threshold energies demonstrate that ribose and lyxose are preferentially complexed at the C_2–C_3 *cis*-diol function whereas arabinose and xylose are esterified at the C_1–C_2 hydroxyl groups. No evidence was found of the existence in the pentose–borate gas phase ionic population of the tridentate structures reported in solution by recent NMR studies.

The stronger affinity of ribose for borate is not confirmed, whereas the ribose probiotic rule can be explained by considering its peculiar capability, among the pentoses investigated, to complex the borate anion at the C_2–C_3 hydroxyl groups almost completely, thus permitting the subsequent stages of nucleotide assembly, such as phosphorylation and linkage to the nucleobases.

The differences observed in the CAD spectra of the pentose–borate complexes can certainly be taken into account for the purpose of mass spectrometric discrimination in complex mixtures.

Acknowledgments

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