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Note

Differentiation of some underivatised anomeric methyl glycosides by f.a.b. and m.i.k.e. mass spectrometry

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Mass spectrometry using surface ionisation modes is a powerful technique for the structural investigation of oligosaccharides.

Fast-atom bombardment[1] (f.a.b.) appears to be the most suitable ionisation mode for the analysis of underivatised oligosaccharides, since information on molecular weight and sequence can be obtained[2,3] from either the positive or negative mode. However, differentiation of underivatised methyl α- and β-glycosides by mass spectrometry still remains a problem.

Recently, we have described[4,5] a method for the differentiation of the aldohexoses which employs the f.a.b. ionisation mode (Scheme 1). A cation-bound species[6] $(S–cat–m)^+$ is generated which is then selected by the magnetic field, and its unimolecular decomposition products are recorded by scanning the electrostatic sector (m.i.k.e. analysis) of a reverse-geometry mass spectrometer. Two kinds of fragment ions, $(S + cat)^+$ and $(m + cat)^+$, arise and their relative abundances are characteristic of a particular aldohexose.

We have now investigated the scope of this method for the differentiation of anomeric methyl glycosides, namely, methyl α- (**1**) and β-D-glucopyranoside (**2**), and methyl α- (**3**) and β-D-galactopyranoside (**4**).

Fig. 1 shows the m.i.k.e. spectrum of the sodium-bound adduct *m/z* 309 (methyl α-D-glucopyranoside–Na–glycerol)$^+$ generated from **1** and sodium iodide with glycerol as the matrix. As described[4,5] for aldohexoses, two signals were observed at *m/z* 217 and 115, corresponding to (methyl α-D-glucopyranoside + Na)$^+$ and (glycerol + Na)$^+$, respectively. When glycerol was used as the matrix in conjunction with lithium or sodium cations in the absence of glycopyranoside at the target surface, a signal at *m/z* 217 was observed in the m.i.k.e. spectrum of the precursor ion *m/z* 309. Its intensity was 5% of that of the signal corresponding to (glycopyranoside + cat)$^+$ in the m.i.k.e. spectrum of the cationised adduct (glycopyranoside + cat + glycerol)$^+$. However, Fig. 2 indicates that the relative

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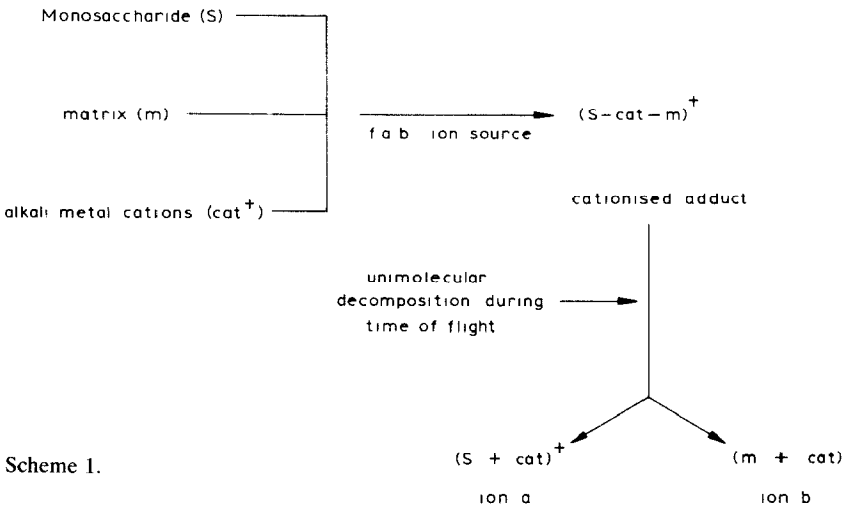

Scheme 1.

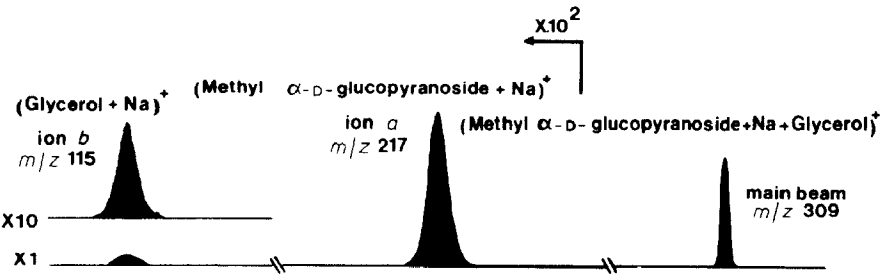

Fig. 1. M.i.k.e spectrum of the cationised adduct (methyl α-D-glucopyranoside–Na–glycerol)$^+$ generated by f.a.b.

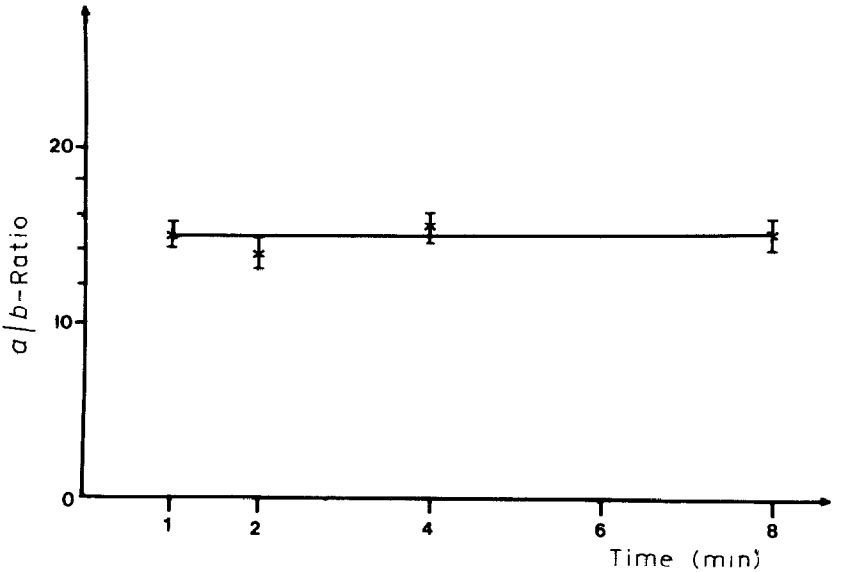

Fig. 2. *a*/*b*-Ratios for the abundance of the ions *a* (methyl α-D-glucopyranoside + Na)$^+$ and *b* (glycerol + Na)$^+$ in the m.i.k.e. spectra of their cationised-bound adduct precursor-ions during their formation.

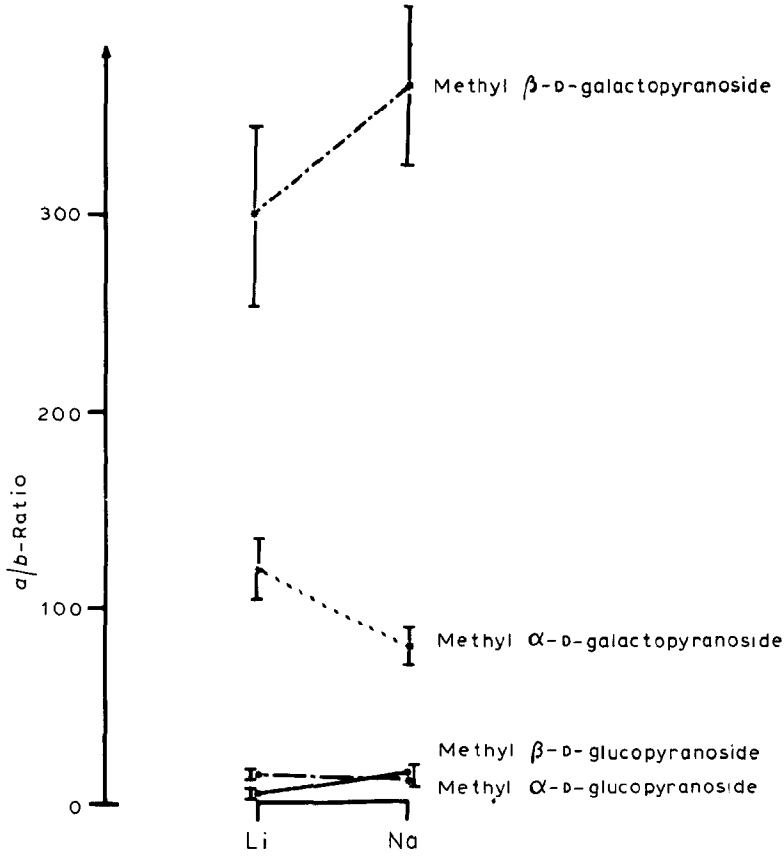

Fig. 3. *a*/*b*-Ratios for the abundance of the ions *a* (α- or β-D-glycopyranosides + cat)$^+$ and *b* (glycerol + cat)$^+$ arising from the unimolecular dissociation of the different cationised species.

abundance of the ions *a* and *b* in Fig. 1 remains almost identical (*a*/*b*-ratio, 15 ±1) during the production of the cationised adduct, thus allowing reproducibility of the measurements.

M.i.k.e. spectra of the cationised-bound adducts of **1–4** have been recorded. The intensity ratios corresponding to the ions *a* and *b* are summarised in Fig. 3. From these values, mainly two phenomena are observed. Galactopyranosides have a higher affinity for Li^+ and Na^+ than do glucopyranosides. Similar results have been obtained[4,5] for D-glucose and D-galactose. The β anomers have the higher affinity for Li^+; this differentiation is more marked for the galactopyranosides.

Work is in progress on other glycosides, aimed at establishing a correlation between the complexing ability of an alkali-metal cation by a sugar molecule in the gas phase and the conformation of the sugar.

EXPERIMENTAL

F.a.b. and f.a.b./m.i.k.e. mass spectra were obtained with a Micromass VG ZAB 2F mass spectrometer. Glycerol (0.5 μL) was deposited on the target by using a Micropettor SMI Polylabo, followed by M methyl glycopyranoside (0.5 μL) and 0.1M alkali-metal iodide (0.5 μL) with 0.5-μL microcaps (Drummond).

M.i.k.e. spectra were recorded with a scan speed of 30 s over the energy range 8 kV, corresponding to transmission of the main beam, and the energy value corresponding to the transmission of ion *b* (Scheme 1). In order to increase the reproducibility of the peak height, the scan speed was reduced by a factor of 10 several eV before the energy corresponding to the transmission of ions *a* and *b*.

REFERENCES

1 M. BARBER, R. S. BORDOLI, R. D. SEDGWICK, AND A. N. TYLER, *J. Chem. Soc., Chem. Commun*, (1981) 325–326.
2 A. DELL AND C E. BALLOU, *Biomed. Mass Spectrom.*, 10 (1983) 50–56.
3 A. DELL AND C. E. BALLOU, *Carbohydr. Res.*, 120 (1983) 95–111.
4 G. PUZO AND J. C. PROMÉ, *Spectrosc. Int. J.*, 3 (1984) 155–158.
5 G. PUZO AND J. C. PROMÉ, *Anal. Chem.*, in press.
6 G. PUZO AND J. C. PROMÉ, *Org. Mass Spectrom.*, in press.