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Preliminary communication

Observation of ion–molecule reactions of methyl glycopyranosides during chemical-ionisation mass spectrometry

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In the tight ion-source of mass spectrometers, using methane or isobutane as reagent gas, several types of ion–molecule reactions may occur, namely, (*a*) charge transfer; (*b*) hydride transfer; (*c*) dissociative hydride transfer; (*d*) proton transfer from the $[RH]^+$ ion, *e.g.*, $[C_4H_9]^+$, to the sample molecule, *i.e.*, $[RH]^+ + M \rightarrow R + [MH]^+$; and (*e*) reactions that occur at increased pressure in the ion-source. If M is a glycoside, protonation may occur at one of several O-atoms, but the fragmentation of the $[MH]^+$ ions is principally by dissociation of the conjugate acid resulting from protonation of the exocyclic O-atom at the glycosidic C-atom. The glycosyl ion is often the most abundant ion obtained from simple glycosides[1]. Indeed, the earliest c.i.-mass spectrum of methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside[2], with isobutane as reagent gas, did not exhibit a peak corresponding to the $[MH]^+$ ion, but the $[MH{-}MeOH]^+$ ion gave rise to the base peak.

Aliphatic ketones[3] and other polar compounds[4] give, in addition to the $[MH]^+$ ion, $[M_2H]^+$ and $[M_3H]^+$ ions that are not solely proton-bound clusters but, in part at least, are produced by the formation of covalent bonds. Also, methyl α-D-glucopyranoside, when introduced as a solid through the direct-inlet probe, gives spectra that are not readily reproducible[5]. Methyl 2,3,4,6-tetra-*O*-methyl-β-D-galactopyranoside gave[6] ions corresponding to $[M_2H{-}MeOH]^+$, $[M_2H{-}2MeOH]^+$, and $[M_2H{-}3MeOH]^+$, but their abundances were only 1–3% of that of the base peak due to $[MH]^+$ and were "sensitive to changes in the operating conditions".

We have investigated the c.i.-mass spectra, with isobutane as reagent gas, of methyl α-D-arabino-, β-D-arabino-, β-L-arabino-, α-D-lyxo-, β-L-lyxo-, α-D-xylo-, β-D-xylo-, α-D-galacto-, β-D-galacto-, α-D-gluco-, β-D-gluco-, α-D-manno, 6-deoxy-β-D-allo-, 6-deoxy-α-L-galacto-, and 6-deoxy-α-L-manno-pyranoside. A VG Micromass 7070H instrument was used, operating at ~150°, with isobutane at an initial nominal pressure in the ion-source of ~0.5 Torr, an electron energy of 50 eV, and an emission current of 200 μA. The spectra were scanned at intervals of ~3 s and recorded with a VG 2235 Data System. The spectrum of each compound contained peaks corresponding to ions derived from two sub-

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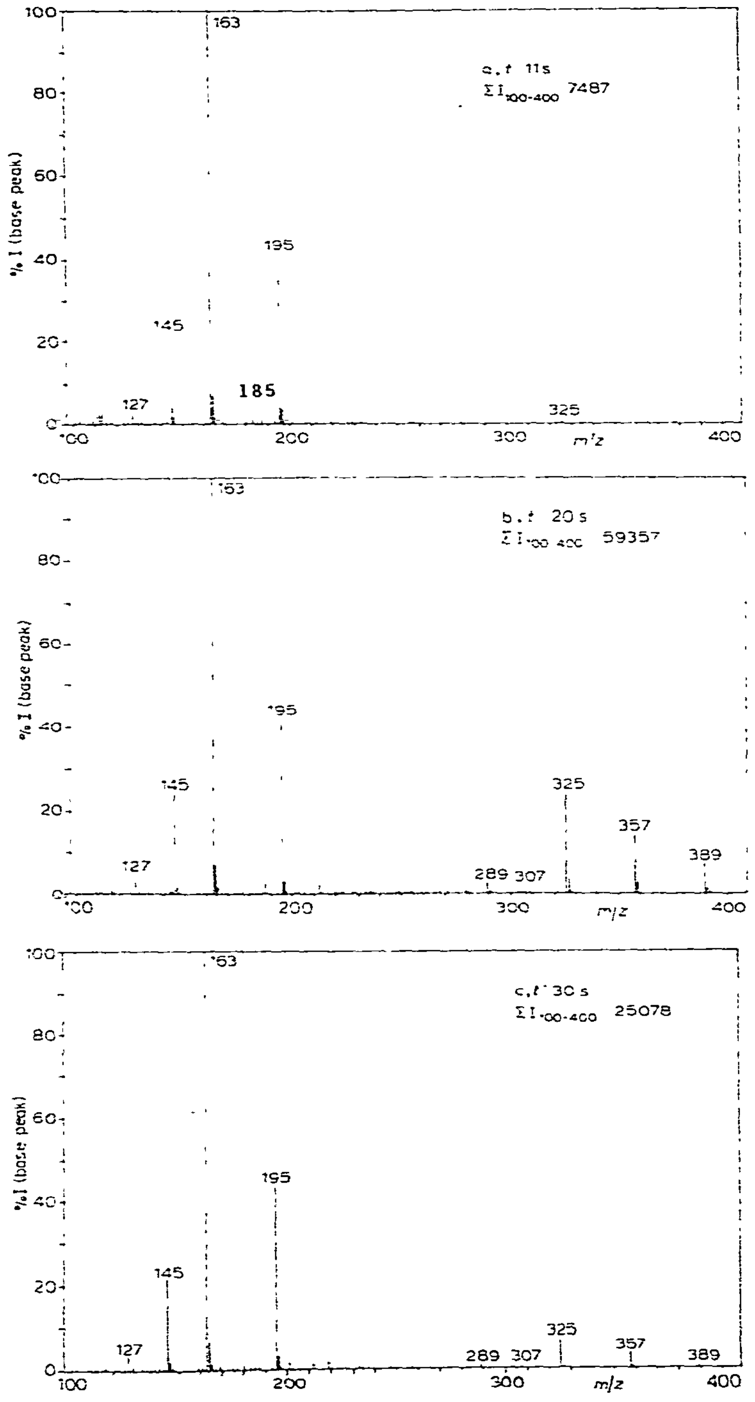


Fig. 1. C.i.-mass spectra of methyl α-D-glucopyranoside. For details, see text.

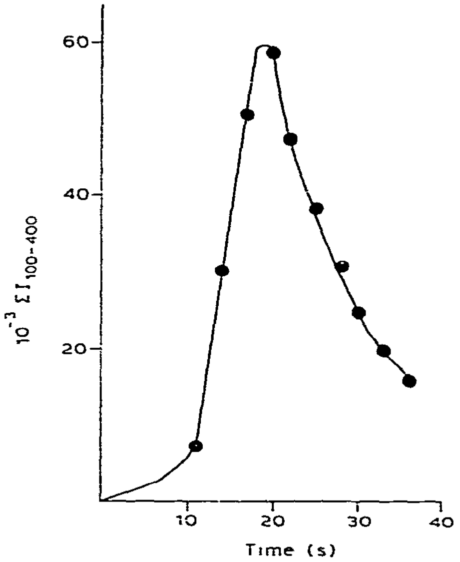
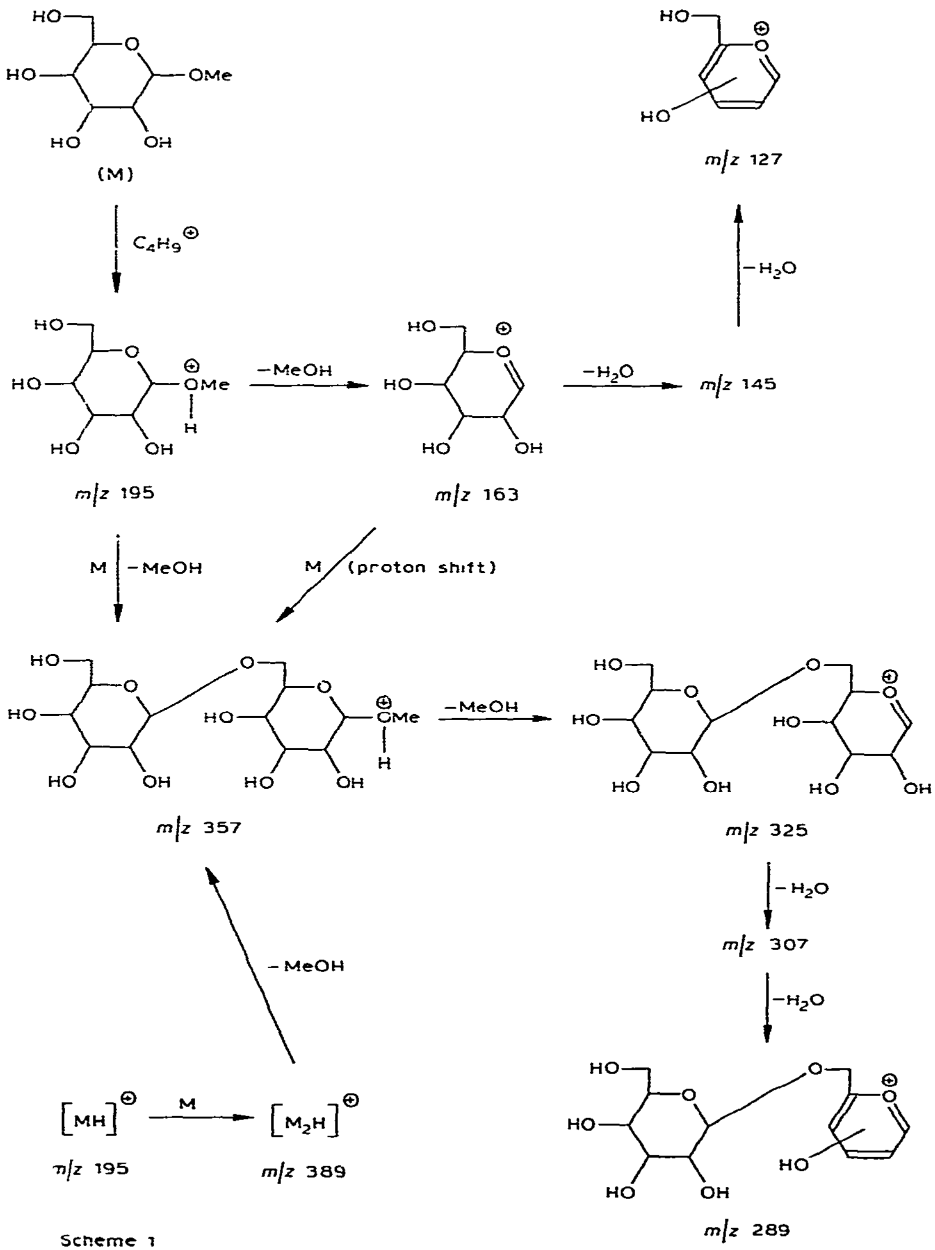


Fig. 2. Total ion-current generated in a mass spectrometer by volatising ~5 μg of methyl α-D-glucopyranoside.

strate molecules. Fig. 1 shows the spectra of methyl α-D-glucopyranoside recorded at ~11 ~20, and ~30 s, respectively, after the introduction of ~5 μg of sample through the direct-inlet probe. Fig. 2 shows the total ion current generated by ions with *m/z* between 100 and 400 over a period of ~36 s. It is apparent that the quantitative changes observed are the result of changes in only one operating condition, namely changes in partial pressure of substrate in the ion-source, occasioned by changes in rate of volatilisation of sample and its gradual removal from the ion-source.

The ions indicated in Fig. 1 with *m/z* 195, 163, 145, and 127 correspond to $[MH]^+$, $[MH-MeOH]^+$, $[MH-MeOH-H_2O]^+$, and $[MH-MeOH-2H_2O]^+$, respectively, whereas those with *m/z* 389, 357, 325, 307, and 289 correspond to $[M_2H]^+$, $[M_2H-MeOH]^+$, $[M_2H-2MeOH]^+$, $[M_2H-2MeOH-H_2O]^+$, and $[M_2H-2MeOH-2H_2O]^+$, respectively. When larger amounts (~10 μg) of sample were introduced into the ion-source, resulting in higher partial pressure of substrate, ions with even higher *m/z* values were sometimes observed, *viz.*, 551 ($[M_3H-MeOH]^+$), 519 ($[M_3H-2MeOH]^+$), 501 ($[M_3H-2MeOH-H_2O]^+$), and 469 ($[M_3H-3MeOH-H_2O]^+$). As the ions derived from two or more substrate molecules are produced in significant quantities only at apparent, high partial-pressure of substrate, they are likely to be the consequence of ion–molecule reactions. The stereochemistry at chiral carbon atoms determines the relative abundances of these ions. For example, at the same total ion current, methyl α-D-glucopyranoside gives the ion $[M_2H]^+$ in larger abundance than does the β anomer.

Likely structures of the ions indicated in Fig. 1 and possible routes for their formation are shown in Scheme 1. A quantitative evaluation of the spectra, also taking into account spectral changes occurring as a result of stereochemical changes in the methyl glycopyranosides, is in progress and is expected to throw light on the routes by which the ions derived from two substrate molecules are produced.



Scheme 1. Ion–molecule reactions of methyl glycopyranosides, and consequential degradations, illustrated for the pyranoside of an aldohexose when the cligomerisation involves the synthesis of a (1 → 6) linkage.

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