THE MASS SPECTRA OF 6-DEOXY-6-HALOGENO-α-D-GLUCOPYRANOSE TETRA-ACETATES*

O. S. CHIZHOV**, A. B. FOSTER, M. JARMAN, AND J. H. WESTWOOD

Chester Beatty Research Institute, Institute of Cancer Research: Royal Cancer Hospital, London S. W. 3 (Great Britain)

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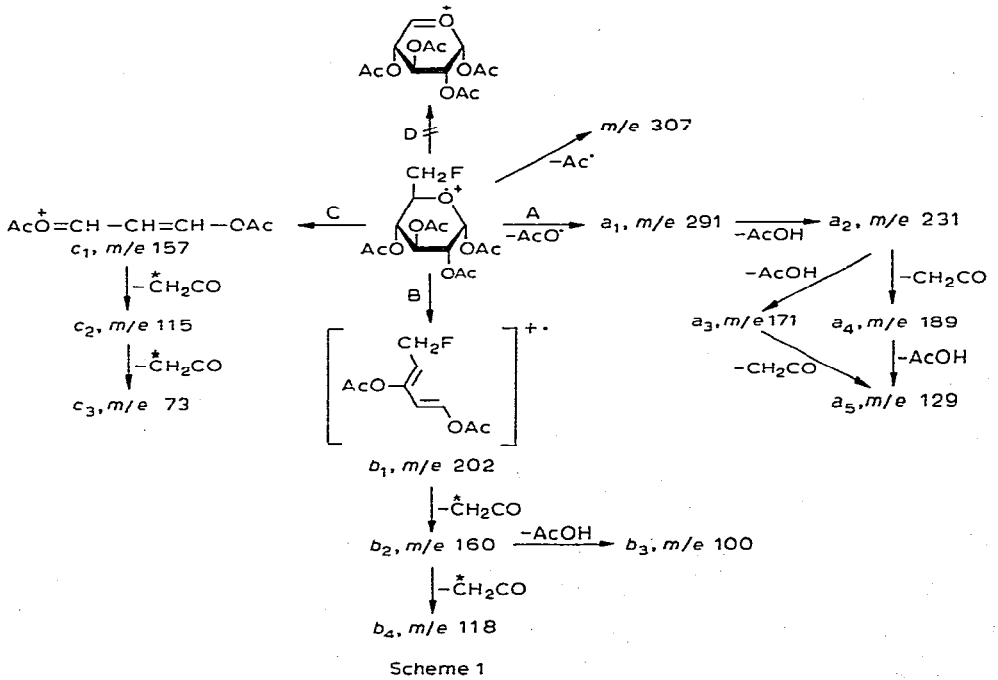
ABSTRACT

The mass spectra of the four 6-deoxy-6-halogeno-α-D-glucopyranose tetra-acetates are discussed in terms of the effect of the nature or the halogen substituent on the fragmentation pathways. The ease with which atomic halogen of hydrogen halide is eliminated from the molecular ion or from fragment ions increases with decreasing



Scheme 1

Scheme 1. Fragmentation pattern for 6-deoxy-6-fluoro-α-D-glucopyranose tetra-acetate (*cf.* ref. 1).

*Dedicated to Professor M. Stacey, C.B.E., F.R.S., in honour of his 65th birthday.

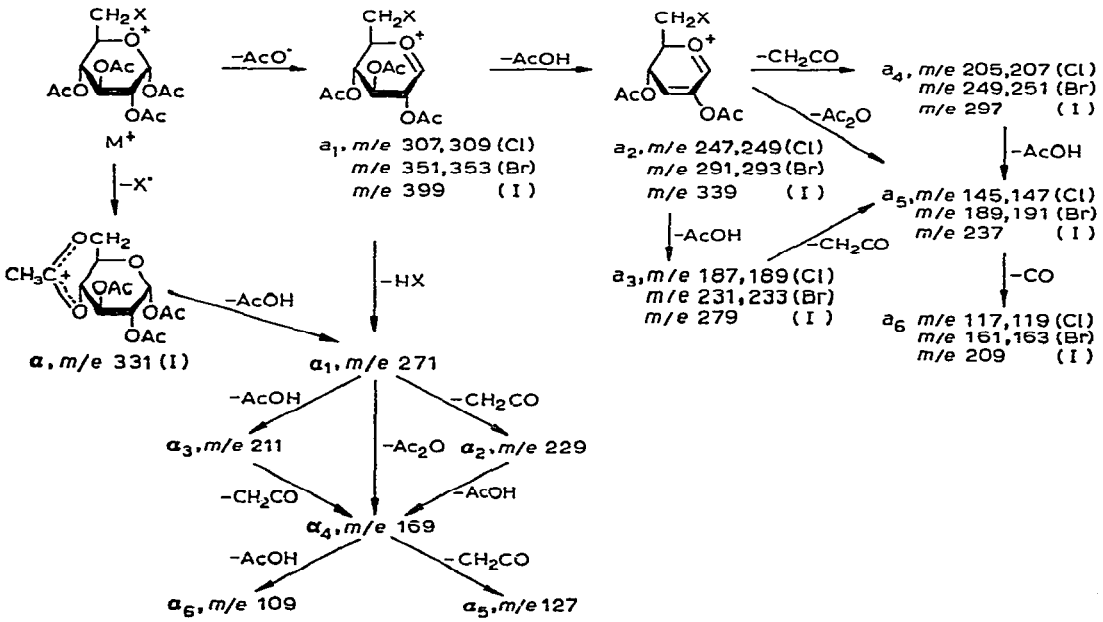
**Visiting Scientist, Mass Spectrometry Laboratory, Institute of Cancer Research. Present address: N. D. Zelinsky Institute for Organic Chemistry, Academy of Sciences of U. S. S. R., Moscow, U. S. S. R.

electronegativity of the halogen substituent. This is the principal trend which differentiates the fragmentation pathways of the four derivatives.

INTRODUCTION AND DISCUSSION

The mass spectra of some acetylated deoxyfluoro-D-hexopyranoses[1] and deoxyfluoro-D-glucitols[2] were described recently with particular emphasis on the effect on the fragmentation pathways of a variously located fluorine substituent. Compared with an acetoxyl group, a fluorine substituent is associated with disfavoured cleavage of the C–C bond in a C(X)–C grouping where X = OAc or F. Thus, for 6-deoxy-6-fluoro-α-D-glucopyranose tetra-acetate, the fragmentation pattern (Scheme 1) resembles that[3] of the hexose penta-acetates, except that pathway *D*, which is initiated by the loss of C-6 as CH_2OAc from the molecular ion, is completely suppressed.

The availability[4] of the 6-chloro, 6-bromo, and 6-iodo derivatives of 6-deoxy-D-glucose permitted an investigation of the influence of the halogen substituent on the mass-spectral fragmentation pattern. The α-tetra-acetates of the 6-deoxy-6-halogeno-



Scheme 2

Scheme 2. Fragment ions of pathway *A* for the 6-chloro (1), 6-bromo (2), and 6-iodo (3) derivatives of 6-deoxy-α-D-glucopyranose tetra-acetate. The halogen associated with particular fragment ions is indicated in brackets after the appropriate *m/e* values. The fragment nomenclature used in Schemes 2 and 3 corresponds to that used in Scheme 1 and ref. 1. The mass spectra for 1–3 are shown in Figs. 1–3; ions containing chlorine and bromine each give rise to two peaks due to the presence of the pairs of isotopes ^{35}Cl, ^{37}Cl and ^{79}Br, ^{81}Br.

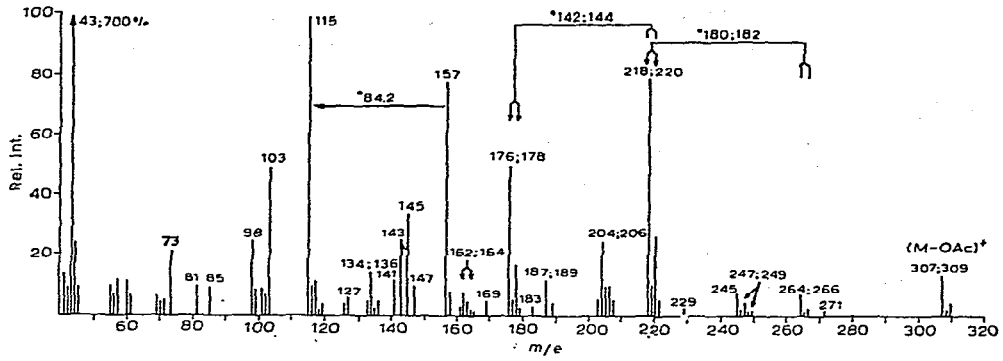


Fig. 1. Mass spectrum of 6-chloro-6-deoxy-α-D-glucopyranose tetra-acetate (1).

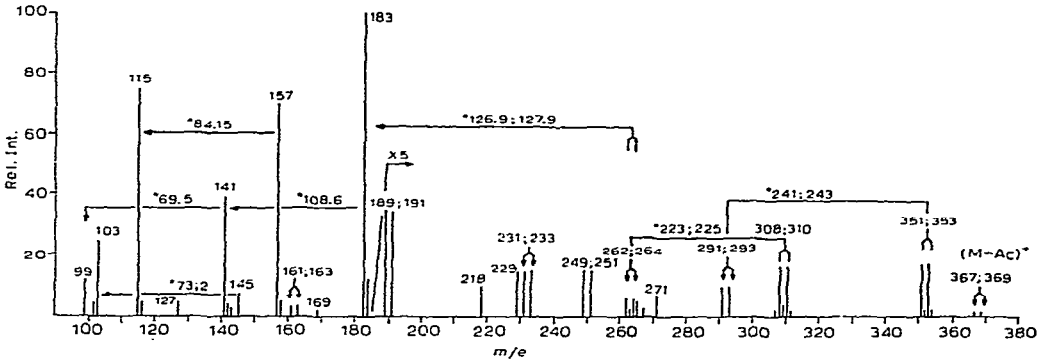


Fig. 2. Mass spectrum of 6-bromo-6-deoxy-α-D-glucopyranose tetra-acetate (2).

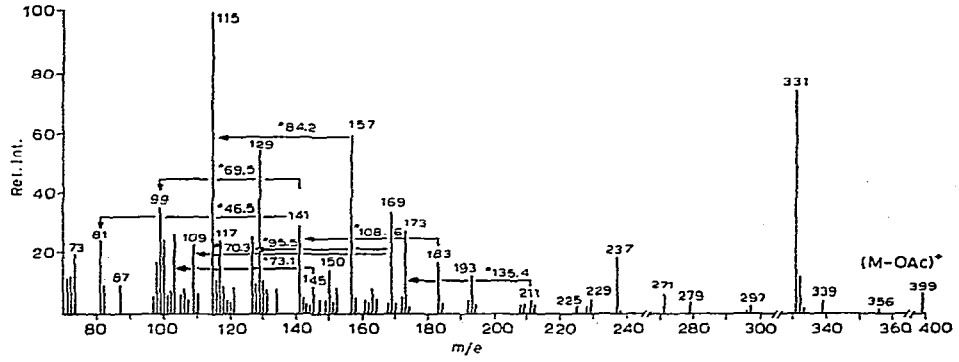


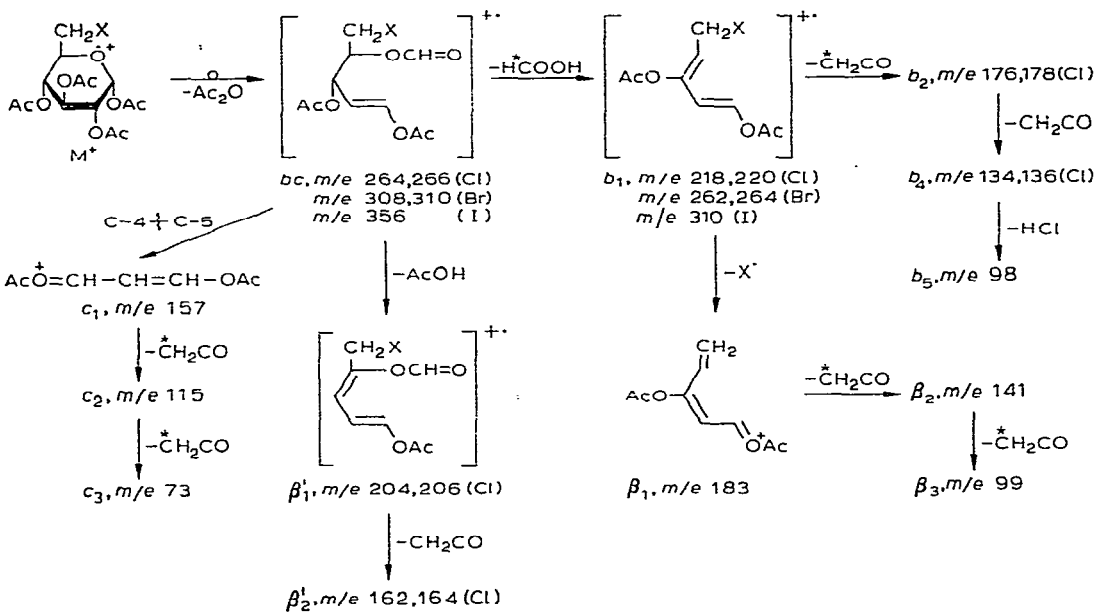
Fig. 3. Mass spectrum of 6-deoxy-6-iodo-α-D-glucopyranose tetra-acetate (3).

D-glucopyranoses are known compounds[5–7]. An analysis of the fragmentation patterns of acetylated glycopyranosyl halides will be published elsewhere.

The fragmentation pathways of the 6-chloro (1), 6-bromo (2), and 6-iodo (3)

derivatives, which are depicted collectively in Schemes 2 and 3, have several features in common with those (Scheme 1) of 6-deoxy-6-fluoro-α-D-glucopyranose tetra-acetate. However, Schemes 2 and 3 contain additional fragments specific to one or more of the halogen derivatives **1–3**.

Numerous fragment ions associated with pathway *A* (Scheme 2) of the halogeno derivatives **1–3** are not formed from the 6-fluoro analogue (Scheme 1). The elimination of hydrogen halide from the fragment ions α_1, leading to the fragment ions α_1–α_6, occurs only for compounds **1–3**. The loss of atomic halogen from the molecular ion, to give the fragment ion α, is unique to the iodo derivative **3**.



Scheme 3

Scheme 3. Fragment ions of pathways *B* and *C* for the 6-chloro (**1**), 6-bromo (**2**), and 6-iodo (**3**) derivatives of 6-deoxy-α-D-glucopyranose tetra-acetate.

The initial stages of pathways *B* and *C* (Scheme 3) are similar for each of the halogeno derivatives. The elimination of acetic anhydride from the molecular ion gives a fragment ion (*bc*) which is the immediate precursor of each pathway. The fragment ions c_1–c_3, which are formed by cleavage of the C-4–C-5 bond followed by the successive elimination of two molecules of ketene, are amongst the most abundant in the spectra of all four halogeno derivatives.

In contrast to pathway *C*, pathway *B* is markedly influenced by the nature of the halogen substituent. One of the two fragmentation pathways leading from the *bc*-ion, namely, the elimination of acetic acid and ketene to give the fragment ions β'_1 and β'_2, is operative only for the chloro derivative **1**. The other pathway leads, through loss of formic acid, to the b_1-ion. The further behaviour of this ion depends upon the

nature of the halogen substituent. The fluorine- and chlorine-containing ions successively eliminate two molecules of ketene and a molecule of hydrogen halide. Those containing chlorine, bromine, or iodine expel a halogen atom followed by two molecules of ketene. The resulting ions (β_1, β_2, and β_3) are particularly prominent in the spectrum of the bromo derivative **2**, whereas, for the chloro derivative **1**, their abundance is very low.

As for the 6-fluoro derivative, pathway *D* of fragmentation, exhibited by the hexose penta-acetates, does not occur for the other halogen derivatives **1**–**3**.

With only one major exception, namely, the unique expulsion of acetic acid from the *bc*-ion of the chloro derivative **1**, the difference between the various fragmentation pathways reflects the tendency towards expulsion of hydrogen halide or atomic halogen with increasing electronegativity of the halogen substituent. These processes are particularly important for the bromo (**2**) and iodo (**3**) derivatives (*cf.* ref. 8). In contrast, the four halogeno derivatives were similar, in that the presence of the halogen substituent at position 6 prevented cleavage of the C-5–C-6 bond. For the iodo derivative **3**, this effect probably reflects the ease with which atomic iodine was lost from the molecular ion rather than the effect of the iodine substituent on the strength of the C-5–C-6 bond.

The results reported herein illustrate the utility of carbohydrate molecules for studying the influence of substituent effects on mass-spectral fragmentation patterns.

EXPERIMENTAL

Mass spectra were obtained by the direct-insertion procedure with an A.E.I. MS-12 spectrometer operating at 70 eV with an ion-source temperature of 80–90° and a trap current of 100 μamps.

Compounds **1** and **2** were obtained by treatment of the corresponding 6-deoxy-6-halogeno-D-glucoses[4] with acetic anhydride–pyridine in the conventional manner. Compound **3** was obtained by boiling a solution of **2** in *N*,*N*-dimethylformamide containing an excess of sodium iodide for 3 h. The physical constants of the tetra-acetates accorded with the published data[5–7].

ACKNOWLEDGMENTS

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