The Fragmentation of Some Tetra-acetylglucosides induced by Electron Impact

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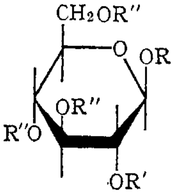
The mass spectra of few glycosides or their esters have been recorded in the literature.[1–3] We have investigated in some detail the fragmentation of some phenolic tetra-acetyl-β-D-glucosides (I; R = aryl, R′ = R″ = Ac).[4]

In every case the strongest peak is at *m/e* 43 (CH_3CO^+) and a weak parent molecular ion (M^+) can be detected, except where R is nitrophenyl when the highest mass peak detected corresponds to loss of NO from M^+. The most abundant ions correspond to two series those (A) derived from the acetylated sugar moiety and the remainder (B) arising from the aglucone (ROH). In the Table the percentage fraction (*P*) of the total ion current carried by ions of type B is given. When R is *o*-, *m*-, or *p*-nitrophenyl type B ions are not observed. Otherwise $\log_{10}P$ correlates reasonably with the Hammett σ-constant[5] for the substituent attached to the phenyl ring except for the two acetoxy-compounds. This correlation also fails when R is 2-naphthyl; σ-constants are not available for the other polynuclear aromatic substituents.



(I)

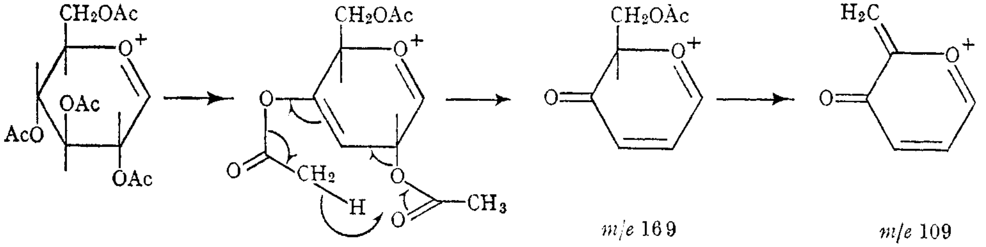
The most interesting ions of series A occur at *m/e*-values of 331, 271, 229, 211, 187, 169, 127, 109, 81, *i.e.*, they form the series of pyronium ions identified in the spectra of pentose acetates by Biemann, DeJongh, and Schnoes.[2] Other fragment ions which predominate in the spectra of alkyl glycosides are weak or absent.

TABLE

Fraction (P) *of total ion current carried by aglucone ions*

Aglucone	*P* %	σ
Phenol	4·7	0
o-Cresol	6·1	—
p-Cresol	8·3	−0·17
5-Hydroxyindane	12·6	−0·26
p-Bromophenol	3·6	0·23
p-Methoxyphenol	9·9	−0·27
m-Acetoxyphenol	5·3	0·39
p-Acetoxyphenol	8·1	0·31
m-Hydroxyacetophenone ..	3·0	0·31
p-Hydroxybenzaldehyde ..	3·3	0·22
o-Hydroxybenzyl alcohol ..	7·4	—
o-Nitrophenol	0	—
m-Nitrophenol	0	0·71
p-Nitrophenol	0	0·78
1-Naphthol	11·7	—
2-Naphthol	11·5	0·17
9-Hydroxyanthracene ..	19·8	—

In the spectrum of phenyl-β-D-glucopyranoside tetra-[$^2H_3$]acetate (I; R = Ph, R′ = R″ = CD_3CO) the phenol molecular ion is shifted to *m/e* 95 to the extent of 80% (correction being made for the presence of 10% undeuterated acetate). This figure is rather larger than that expected (63%) for random abstraction of hydrogen from the sugar residue. A further interesting point is that the ion of *m/e* 109 ($C_6H_5O_2^+$)*, formulated as (III) by Biemann, DeJongh, and Schnoes[2] is not shifted, even partially, to *m/e* 110 as required by the mechanism postulated by those workers.[6] The ion also has *m/e* 109 in the spectrum of *p*-nitrophenyl-β-D-glucopyranoside 2-[$^2H_3$]-acetate 3,4,6-tri-[$^1H_3$]acetate (I; R = *p*-nitrophenyl, R′ = CD_3CO, R″ = CH_3CO). A metastable ion at *m/e* 105·4 corresponds to the loss of 102 m.u. (CH_3CO_2H + CH_2CO) from *m/e* 271 in the undeuterated compounds. Models show that a one-step process such as that given below is feasible. Deuteration does however result in a shift of the *m/e* 169 peak to 172 and 173. The latter ion evidently cannot decompose to the ion (III) and must have a structure different from that of the deuterated ion corresponding to (II).



m/e 331 *m/e* 271 *m/e* 169 (II) *m/e* 109 (III)

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*Confirmed by high-resolution studies.

[1] R. I. Reed, W. K. Reid, and J. M. Wilson, "Advances in Mass Spectrometry", ed. R. M. Elliott, Vol. II, Pergamon, London, 1962.

[2] K. Biemann, D. C. DeJongh, and H. K. Schnoes, *J. Amer. Chem. Soc.*, 1963, **85**, 1763; D. C. DeJongh and K. Biemann, *ibid.*, p. 2289.

[3] M. von Ardenne, R. Tümmler, E. Weiss, and T. Reichstein, *Helv. Chem. Acta*, 1964, **47**, 1032; G. Spiteller, *Z. analyt. Chem.*, 1963, **197**, 1.

[4] An A.E.I. MS9 mass spectrometer was used, ionizing voltage 70 ev. Samples were introduced by the direct insertion (probe) technique.

[5] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191; D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[6] Biemann *et al.* introduced their samples through a heated stainless-steel inlet. They found a partial shift of the ion *m/e* 109 to 110.