

Substituent Effects in the Field Ionisation Mass Spectra of Aryl *O*-Glucosides

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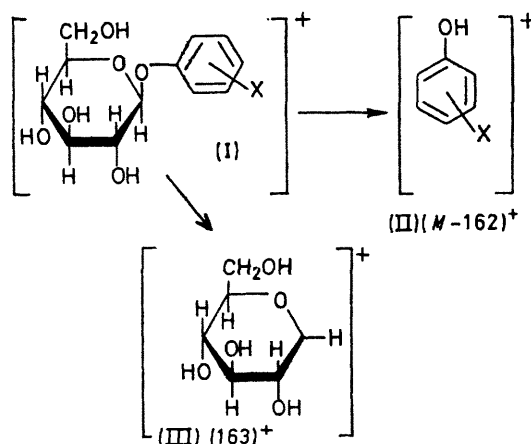
Summary Field ionisation mass spectrometry of substituted aryl *O*-glucosides demonstrates that cleavage and rearrangement reactions occur at the glucosidic bond, and using the Hammett relationship $\log Z/Z_0 = \rho\sigma$ may be correlated to give $\rho + 0.7$ for rearrangement and $\rho + 2.0$ for cleavage.

ATTENTION has recently been given to substituent effects in the electron impact m.s. of aromatic compounds.^{1,2} Here, even at low energies, secondary fragmentation is a frequent complication, and for this reason we have used a 'softer' means of ionisation. Under field ionisation (FI) conditions we find that substituted phenolic glycosides (I) fragment to yield, in addition to the molecular ion and its protonated analogues ($M + 1$, $M + 2$), the ions (II) (rearrangement) and (III) (cleavage) as the major species.

The action of ionising radiations on substituted aryl *O*-glucosides in the solid state yields *D*-glucose and the corresponding phenol after dissolution of the irradiated solid in water.³ The product ions observed during FI mass spectrometry would account for this behaviour and additionally indicate a reasonable analogy between the two processes.

The influence of the substituents in the aglycone on the intensities of the ions (II) and (III) can be rationalised by

considering the rates of reactions leading from (I) to (II) and (III). Using a kinetic approach to mass spectra,¹ the ratios $(M - 162)^+/(M)^+$ and $(163)^+/(M)^+$ relative to



the identical process in the unsubstituted phenyl β -*D*-glucoside can be considered directly proportional to the rate constants of processes (I) \rightarrow (II) and (I) \rightarrow (III). A plot of these ratios (Table) against the appropriate constant

in the Hammett equation ($\log Z/Z_0 = \rho\sigma$)^{4,5} is linear and gives ρ values of +0.7 for the reaction leading to (II) and +2.0 for the formation of (III). Observance of such a relationship indicates a common route of formation for all the ions studied, except when the substituents are nitro-groups, where significant deviations are apparent. Here rearrangement with addition of hydrogen at the nitrogen centre is probable, with the result that the balance between rearrangement and cleavage would be changed. This behaviour is observed in both electron impact m.s. and photochemical reactions of substituted nitro-aromatic compounds.⁶

At present the significance of the ρ values derived from electron impact data is not clear. As far as we are aware, the present values are the first to be derived from FI measurements.

Relative intensities of ions (II) and (III) in the FI mass spectra of substituted phenyl β -D-glucosides^a

$$Z(\text{II}) = \frac{(M-162)^+/(M)^+}{(M-162)^+_o/(M)^+_o}; \quad Z(\text{III}) = \frac{(163)^+/(M)^+}{(163)^+_o/(M)^+_o}$$

X	$(M-162)^+/M^+$	$(163)^+/(M)^+$	Z(II)	Z(III)
<i>o</i> -NO ₂	3.46	1.34	46.1	79.0
<i>p</i> -NO ₂	2.6	0.71	34.6	41.7
<i>m</i> -NO ₂	1.75	1.47	23.4	86.4
<i>p</i> -CN	5.1	1.65	68	97.0
<i>m</i> -Cl	2.84	2.4	37.9	141.0
<i>p</i> -Br	3.66	0.68	48.9	40.0
<i>p</i> -Cl	3.34	0.39	44.5	22.9
H	0.075	0.017	1.0	1.0
<i>o</i> -Me	1.56	0.058	20.4	3.4
<i>p</i> -CH	1.32	0.077	17.6	4.5
<i>p</i> -OMe	1.2	0.04	16.0	2.4

^a Measured on an A.E.I. MS9 Mass Spectrometer: source temperature 80°; ionising voltage 11 kv (razor blade emitter).

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