Tetrahedron Letters No. 27, pp 2377 - 2380, 1974. Pergamon Press. Printed in Great Britain.

FIELD DESORPTION MASS SPECTROMETRY OF SODIUM AND POTASSIUM SALTS

D.E. Games, M.P. Games, A.H. Jackson, A.H. Olavesen, M. Rossiter,
and P.J. Winterburn,
Departments of Chemistry and Biochemistry, University College, P.O. Box 78,
Cardiff, CF1 1XL.

(Received in UK 18 April 1974; accepted for publication 30 May 1974)

The utility of field desorption (FD) mass spectrometry in the analysis of thermally labile and involatile compounds is now well documented[1]. Beckey and co-workers have also shown that the technique is applicable to alkali metal salts of acetic acid[2], nucleotides[3] and amino acids[4]. More recently Schulten has applied the technique to the sodium salts of glucose phosphates[5] and glucuronides[6] and Brent and Bursey[7] have shown its utility in studies of quaternary ammonium salts.

We have studied the F.D. spectra of the potassium salts of some alkyl sulphates and cyclohexylphenyl sulphate(1), the sodium salts of stilbestrel glucuronide(2), cortisone sulphate(3), deoxycholic acid(4a), taurodeoxycholic acid(4b), dehydrocholic acid(5), glycocholic acid(4c), taurocholic acid(4d), taurochenodeoxycholic acid(4e) and cyclic adenosine monophosphate(6). The spectra were obtained from solutions of the salts in water, with the addition of some methanol or acetone. In most cases ions were present which enabled ready identification of the molecular species and in a number of cases structurally useful fragment ions were also present.

The potassium salts of *n*-hexyl, *n*-decyl and *n*-undecyl sulphates all showed quasi-molecular [M+K$^+$] ions at *m/e* 259, 315 and 329 respectively and no fragment ions. Similar behaviour was observed for the potassium salt of cyclohexylphenyl-4-sulphate(1)

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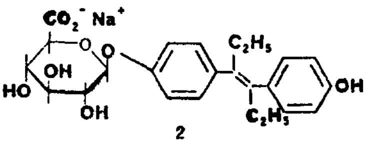

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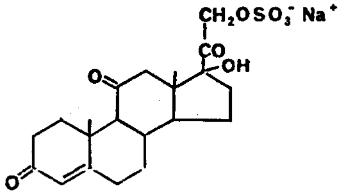
and the sodium salt of diethyl stilbestrol glucuronide(2) quasi-molecular ions being present at m/e 333 $[M+K]^+$ and 489 $[M+Na]^+$ respectively. However, ions were also present at m/e 176 and 268 respectively for cleavages with hydrogen transfer to yield the parent phenols.

The sodium salt of cortisone sulphate(3) shows unusual behaviour at low wire currents. The base peak in its spectrum was at m/e 254 and is assigned to the doubly charged ion $[M+2Na]^{2+}$, other ions were present at m/e 254.5(34%), 255(21%), 255(10%) and 485(8%) $[M+Na]^+$. Higher wire currents increased the intensity of m/e 485 relative to m/e 254. However at 20mA, the highest wire current used, the only ions were at m/e 360(33%) and 342(100%) and they are assigned to loss of the sulphate group with hydrogen transfer, in the first case, and with dehydration and hydrogen transfer in the latter case.



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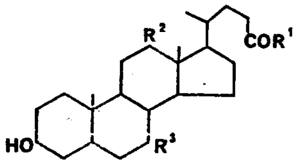
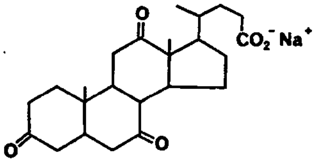
Quasi-molecular ions $[M+Na]^+$ were present for the sodium salts of the bile acids (4a, 5) and their conjugates (4b, 4c, 4d, 4e) and intense doubly charged ions $[M+2Na]^{2+}$ were present in all the spectra. Fig. 1 shows the F.D. spectrum of sodium glycocholate(6a) which is typical. In addition some of the compounds showed $[M+Na-18]^+$ ions and strong ions at higher mass than the quasi-molecular ions. The nature of these latter ions is currently under investigation.





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4 a R^1 = O^- Na^+ ; R^2 = OH ; R^3 = H
b R^1 = $NHCH_2CH_2SO_3^-$ Na^+ ; R^2 = OH ; R^3 = H
c R^1 = $NHCH_2CO_2^-$ Na^+ ; R^2 = R^3 = OH
d R^1 = $NHCH_2CH_2SO_3^-$ Na^+ ; R^2 = R^3 = OH
e R^1 = $NHCH_2CH_2SO_3^-$ Na^+ ; R^2 = H ; R^3 = OH

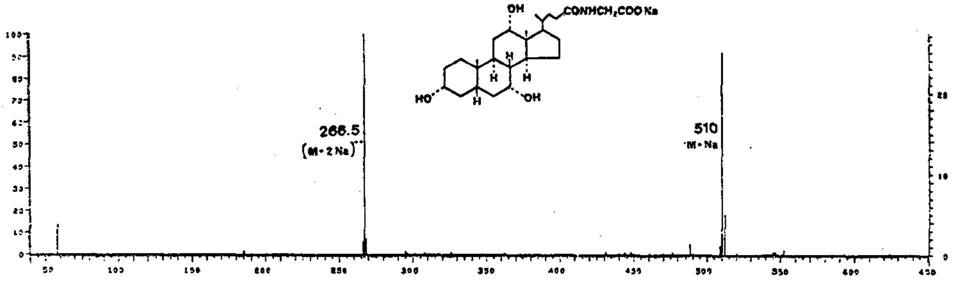

Fig. 1. F.D. Spectrum of Sodium Glycocholate

Fig. 2 shows one of the F.D. spectra of the sodium salt of cyclic adenosine-3',5'-monophosphate(4e). It is similar to the spectrum previously reported[3] for adenosine-5'-monophosphate. A strong $[M+1]^+$ ion is present at m/e 352 and ions at m/e 331 and 318 are assigned to the formation of the protonated phosphate without and with the loss of water respectively. The ion at m/e 135 enables ready identification of the base, being formed by cleavage of the base sugar bonds with hydrogen transfer. Spectra at lower wire currents show the presence of an $[M+Na]^+$ ion at m/e 374 and an ion at m/e 268 arising from cleavages of the 3' and 5' oxygen-phosphorous bonds with proton transfer.

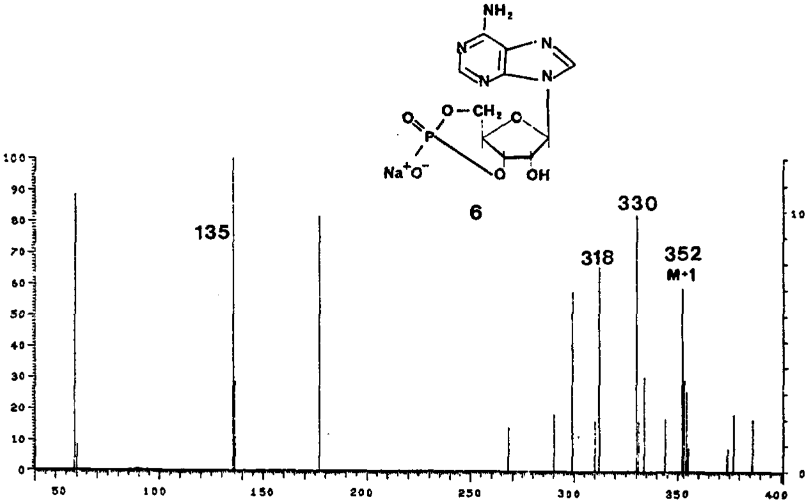

Fig. 2. F.D. Spectrum of the sodium salt of cyclic adenosine-3',5'-monophosphate

Further studies are in progress to examine the utility of F.D. for the detection of compounds of the types described in this paper in biological systems.

Preliminary results with methanol extracts of bile indicate that bile acid conjugates are readily detected in the extracts.

Spectra were obtained using a Varian CH5D mass spectrometer fitted with a combined FD/FI/EI source using benzonitrile activated tungsten emitters. Spectra were obtained via a Varian 620i computer; the data system being calibrated with PFK using the EI source.

We thank the S.R.C. and the Royal Society for financial assistance in the purchase of the mass spectrometer and FD/FI/EI source respectively.

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