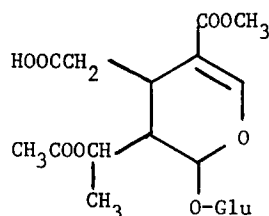


A COMPARISON OF MASS SPECTROMETRIC TECHNIQUES IN THE STRUCTURE ELUCIDATION OF A NON-VOLATILE SECOIRIDOID GLYCOSIDE

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In the past, mass spectrometry has been of limited value for relatively non-volatile materials because the higher mass fragments which may be of greatest significance, including the molecular ion, are not seen. The usual procedure with, for example, plant glycosides or conjugated drug metabolites, has been to derivatise the material in order to render it more volatile. This involves extra effort in finding suitable derivatives and may introduce further ambiguities, as described below. Recent advances in technique have resulted in convenient methods for the obtention of spectra on underivatized materials, and these have been applied as part of the structure elucidation of the new secoiridoid (1), isolated from the stem bark of Nauclea diderrichii (Rubiaceae).



(1)

The techniques which were applied were (a) conventional electron-impact M.S., with and without direct probe insertion (b) chemical ionisation using ammonia (c) trimethylsilylation with E.I.M.S. (d) methylation/acetylation with E.I.M.S. (e) field desorption (f) fast atomic bombardment (Williams et al 1981) (g) desorption-chemical ionisation (Hostettmann et al 1981).

As anticipated, techniques (a) and (b) gave large numbers of low-mass fragments with potentially a large amount of structural information, but no molecular ion. Silylated material gave as the highest mass a fragment  $(M-15)^+$  which was potentially misleading, and the methylation/acetylation product gave an acceptable spectrum, but naturally the presence of the original acetyl group was obscured.

Field desorption gave  $(M+Na)^+$  as well as  $M^+$  and  $(M-H_2O+Na)^+$ ; in certain circumstances the presence of the sodium-augmented fragments could be confusing, although reportedly the greatest disadvantage of FDMS is the time taken in sample preparation. This has been overcome in the recently developed FAB technique, but with the penalty that the number of ions arising as artefacts of the process is greatly increased: these include ions arising from bombardment of glycerol (used in sample preparation) as well as some complex metal combinations. In contrast, D.C.I. gave a clean spectrum with a simple molecular ion, the only disadvantage being a relative lack of fragments in the middle range between the molecular ion and the complex region below  $m/z$  200.

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Williams, D.H., Bradley, C., Bojesen, G., Santikarn, S. and Taylor, L.C.E. (1981) *J. Am. Chem. Soc.* 103: 5700-5704

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