

KEYNOTE HISTOTICAL

CHEMICAL STRUCTURE DETERMINATION BY MASS SPECTROMETER : AN HISTORICAL PERSPECTIVE

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In the 1960's there was an explosive growth in the application of nuclear magnetic resonance and mass spectrometry to organic chemistry which revolutionised research in to the elucidation of complex chemical structures.

At the Division of Coal Research, CSIRO Sydney, in 1958 we foresaw the potential of these techniques and had orders placed for a Varian NMR machine and an Atlas CH4 Mass Spectrometer. Both machines were delivered by 1961 and we set to work studying the interpretation of NMR and mass spectra in terms of chemical structure.

Our work in mass spectrometry following that time will be considered in three main areas.

- 1) the study of families of compounds both organic and metal-containing, sometimes isotopically labelled to assist the interpretation in terms of ion reactions and ion structures. Included was the discovery of metal valency effects, the importance of hydrogen migration, the essential need to use proper ion symbolism and 'electron bookkeeping' and deuterium labelling by direct insertions of D₂O into the mass spectrometer.
- 2) The use of our developed understanding of the mechanisms of ion fragmentation to help solve important unresolved structural problems by mass spectrometry for the first time. For example with the triterpenes, alkaloids, purine (including zeatin the first pure cytokinin cell growth factor isolated), cyclodepsipeptide and the complex fungal metabolite sporidesmin C and coordination compounds.
- 3) we developed metal-catalysed hydrogen-exchange methods to specifically label aromatic and heterocyclic compounds and in our studies of metal coordination compounds we discovered the basic and unique phenomenon of intramolecular chelate linkage isomerism.

The above work and access to problems and materials was made possible by the enthusiastic collaboration of research workers in both Australia and New Zealand and my friends and colleagues in CSIRO, especially C G McDonald and M J Lacey.