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THE DISULFIDE LINK BETWEEN TWO CYS RESIDUES IN PEPTIDES CAN BE IDENTIFIED BY NEGATIVE ION MASS SPECTRROMETRY.

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The isolation of a number of potent disulfide containing neuropeptides from the *Crinia* genus of Australian frogs has enabled us to investigate the negative fragmentations of the disulfide link. Positive ion mass spectrometry is not particularly effective in determining the position of disulfide links in peptides or proteins. In contrast, the presence of a pronounced $[(M-H)^- - H_2S_2]$ fragment anion, immediately identifies the presence of the disulfide link. MS/MS data from this fragment anion allows the determination of the amino acid sequence of the peptide using the normal α and β backbone cleavages.¹

The disulfide cleavage will be illustrated by the negative ion mass spectra of a number of bioactive peptides. Theoretical calculations have been used to investigate the mechanisms of the major negative ion disulfide cleavages.