

Table 1. Tabulated m/z values of predicted and observed peptide fragments and β -elimination products

Open Cys9-Cys60		
Fragment	Predicted mass, Da	Observed mass, Da
Ala ₁ -Cys ₁₈	772.88	N.D.
itz ₉ -Lys ₅₉	5,086.94	5,080.695*
itz ₆₀ -Ala ₈₂	2,411.74	2,413.79
Ala ₁ -(β Cys ₉)Lys ₅₉	5,764.72	5,770.79
itz ₉ -(β Cys ₆₀)Ala ₈₂	7,421.57	7,447.43 [†]
Open Cys18-Cys54		
Ala ₁ -Tyr ₁₇	1,857.1	1,857.04
itz ₁₈ -Gln ₅₃	3,454.1	3,436.10* [‡]
itz ₅₄ -Ala ₈₂	2,957.4	2,956.85
Ala ₁ -(β Cys ₁₈)Gln ₅₃	5,237.05	5,238.07*
itz ₁₈ -(β Cys ₅₄)Ala ₈₂	6,336.36	N.D.
Open Cys19-Cys45		
Ala ₁ -Cys ₁₈	1,961.23	N.D.
itz ₁₉ -Gly ₄₄	2,508.92	2,509.55*
itz ₄₅ -Ala ₈₂	3,800.42	3,796.94*
Ala ₁ -(β Cys ₁₉)Gly ₄₄	4,394.03	4,409.147 [§]
itz ₁₉ -(β Cys ₄₅)Ala ₈₂	6,233.22	N.D.
Open Cys61-Cys80		
Ala ₁ -Cys ₆₀	5,919.94	5,902.98 [‡]
itz ₆₁ -Asn ₇₉	2,035.24	2,036.25
itz ₈₀ -Ala ₈₂	3,16.38	N.D.
Ala ₁ -(β Cys ₆₁)Asn ₇₉	7,878.07	7,894.07 [§]
itz ₆₁ -(β Cys ₈₀)Ala ₈₂	2,274.51	N.D.

Fragments highlighted in gray are unique to a particular fingerprint. N.D., not detected; itz, iminothiazolidinyl carboxyl residue. Cys_x-Cys_y designates the disulfide bond that is reduced in the singly reduced and cyanylated species. Ala₁-(X_{x-1}), itz_x-X_{y-1}, and itz_y-Ala₈₂, designates the S-cyanil cleavage products. Ala₁-(β Cys_x)-X_{y-1} and itz_x-(β Cys_y)-Ala₈₂ designate the β -elimination products. β Cys_x and β Cys_y refer to the position of the Cys modified by the β -elimination reaction. X = any amino acid residue; subscript symbols refer to the position of designated singly reduced and cyanylated Cys residues.

*Denotes that both the oxidized and non-oxidized M22 are detected.

†The ion detected is as an adduct with Na^+ .

‡The ion detected has lost H_2O .

§Only the oxidized M22 is detected.