

Figure 1: UPLC/Q-ToF ESI MS (E) and MS/MS (A – D) Total Ion Chromatograms

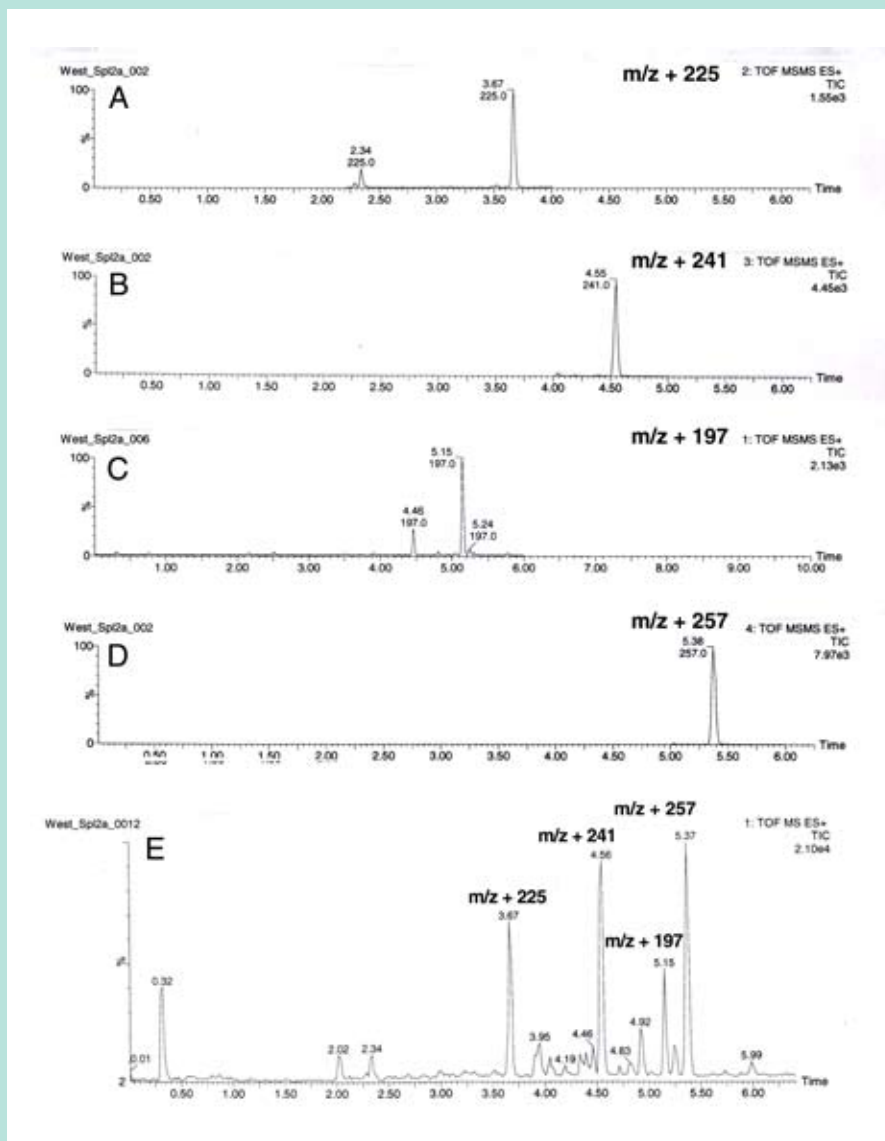


Figure 2: Ion Spectra of the Four Major Extractable Peaks

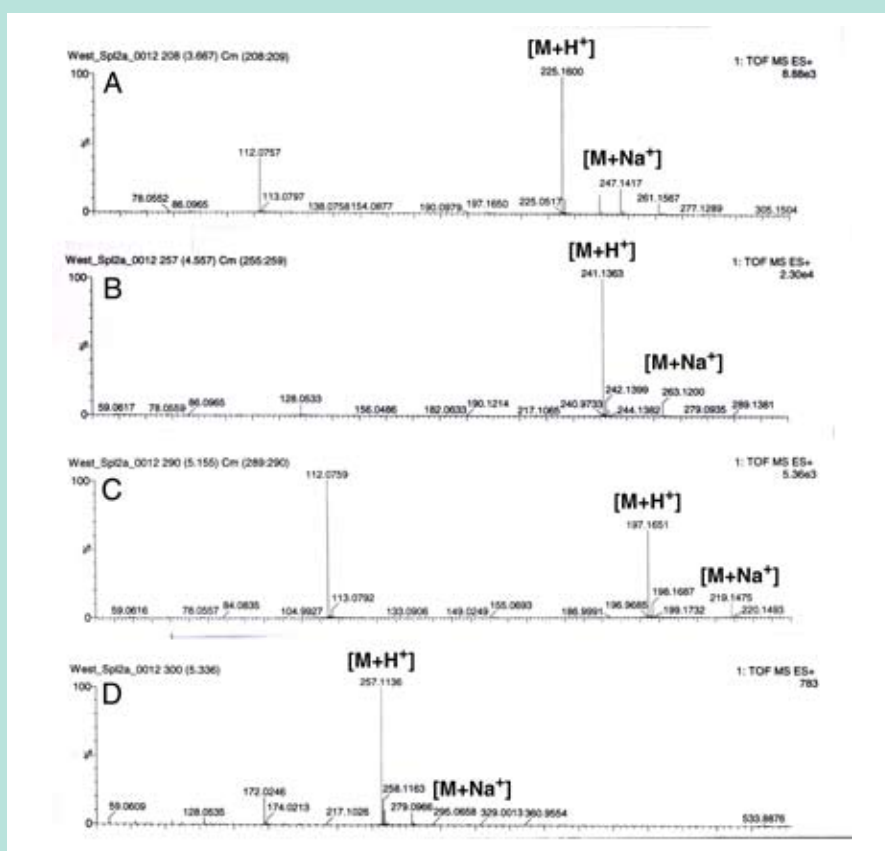


Table 2: Mass Difference between Sulfur and Oxygen

Measured Mass	Difference	Measured Mass	Difference
257.1136	15.9773	241.1363	15.9763
241.1363		225.1600	
S	31.9721	S&O Difference	15.9772
O	15.9949		

The four molecular ions were further analyzed by CID MS/MS to acquire fragment ion spectra (Figure 3) for structural elucidation. Again, 241 and 257 have a common fragment ion with an m/z of 128 of which the isotope pattern indicates sulfur atom(s). Also, the difference of 112.0760 and 128.0529 is 15.9769, a difference of Sulfur and Oxygen which suggests that Sulfur and Oxygen might be the only difference and they may be in the same position in the molecule. In addition, all the four have a common fragment ion with an m/z of 69. Therefore, the four major peaks are structurally related closely.

With all this information, elemental analysis became much easier. Table 3 shows the settings for single mass (for molecular ions) and multiple mass (for MS/MS fragment ions). Table 4 shows the results of elemental analysis.

Table 3: Parameter Settings for Elemental Analysis

Elemental Analysis	Mass Error Tolerance	DBE		Selected Filters	Elements Used				
		Min	Max		C	H	N	O	S
Single Mass*	10 ppm	-1.5	50	None	0-50	0-100	0-10	0-10	0-2
Multiple Mass**	4.0 mDa	-1.5	50	None	0-11	0-21	0-2	0-2	0-2

* For molecular ions. ** For fragment ions.

The results indicate that all of the four major aqueous extractables were derived from a sulfur-containing curing agent (Figure 4). The fragment ions in the MS/MS spectra are explained in Figure 5.

In the aqueous extracts, an Oxygen-Sulfur exchange reaction converting the thio-oxo group(s) into acetyl group(s) was observed under room temperature (Figure 6). The favorable direction was found to be from thio-oxo group to acetyl group which is more stable. Higher temperature promotes this hydrolysis reaction toward acetylation.

Table 4: Elemental Analysis Results

R.T. (min)	Normalinal m/z*	Calculated Mass**	Measured Mass	mDa	PPM Error	DBE	iFTI	Formula
3.667	225	225.1603	225.1600	-0.3	-1.3	3.5	50.7	C12H21N2O2
		112.0762	112.0760	-0.2	-1.8	2.5	0.1	C6H10NO
		84.0813	84.0816	0.3	3.6	1.5	0.8	C5H10N
		69.0704	69.0706	0.2	2.9	1.5	6.1	C5H9
4.557	241	241.1375	241.1363	-1.2	-5	3.5	187.1	C12H21N2OS
		128.0534	128.0529	-0.5	-3.9	2.5	1.2	C6H10NS
		69.0704	69.0705	0.1	1.4	1.5	4.5	C5H9
5.155	197	197.1654	197.1651	-0.3	-1.5	2.5	7.6	C11H21N2O
		112.0762	112.0765	0.3	2.7	2.5	1.3	C6H10NO
		84.0813	84.0819	0.6	7.1	1.5	0.6	C5H10N
5.336	257	197.1651	197.1651	0.0	0.0	2.5	7.6	C11H21N2O
		257.1146	257.1136	-1.0	-3.9	3.5	0.9	C12H21N2S2
		172.0255	172.0257	0.2	1.2	3.5	41	C7H10NS2
		128.0535	128.0535	0.0	0.0	2.5	14	C6H10NS
		69.0704	69.0707	0.3	4.3	1.5	1.7	C5H9

* Monoisotopic mass, odd and even electron ions.

** The lost electron was not considered in accurate mass calculation.