

Detection of Urushiol Allergens of *Toxicodendron* Genus Using Leaf Spray Mass Spectrometry

Supplementary Information

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A schematic diagram of the experimental setup and a photograph are shown in Figure S1. The technique is similar to paper spray ionization mass spectrometry in which a paper substrate (either chromatographic or simple laboratory filter paper) is used to initiate the ionization of samples while greatly reducing matrix contributions in complex samples. The leaf spray method, however, uses the leaf matter itself as a substrate to ionize compounds specific to a given plant simplifying the analysis process even further. Simply cutting the tip of a leaf in a triangle shape, attaching a copper clip to apply the high voltage, and adding 15 μL of a spray solvent initiates ionization of chemicals present on a leaf.

The urushiols detected from poison ivy leaf samples have been investigated using their CID fragment ion profiles. Assignments of fragment using data from authentic compounds is not possible due to the unavailability of the standards. However, the experimental findings of Draper and coworkers, whose samples were obtained from purified extracts of *Toxicodendron diversilobum* (poison oak), can be used as a reference since the mixture of urushiols was first separated with LC and identified using tandem MS. The product ion MS spectra of three out of six urushiols detected and identified in our measurements are shown in Figure S2. These urushiols at m/z 341, 343 and 345, observed in the mass spectrum at high intensity, show very similar fragment ion profiles to those reported in the literature¹. These urushiols possess C17 hydrocarbon side-chains on the catechol ring with varying numbers of double bonds in the molecule (4, 3, and 2 respectively). The mass of ions also differ by 2 units after the loss of water molecule from one of the hydroxyl groups in the catechol ring (Scheme S1(a)). This mass difference remains

present for the higher mass fragments (e.g. m/z 299 vs. 301 and 303; 285 vs. 287 and 289; 271 vs. 273 and 275.). Therefore, it is deduced that these higher mass fragments are the result of further fragmentation of the ion generated by water loss and may be assigned the tentative structure **I** shown in Scheme S2(a). Lower mass fragments, however, do not demonstrate this 2 unit difference in their masses and most of these low mass fragments are identical in all urushiols. Their structures can be described with structures **II**, **III**, or **IV** in Scheme S1. Among the low mass fragment ions, the prominent fragment ion at m/z 123 has been suggested to be the stable dihydroxytropolium ion¹ shown in Scheme S1(b). The structures of both lower and higher mass fragment ions can be assigned to any of these four possible structures, where the level of saturation of the hydrocarbon side-chain can explain the abundance of the fragment ions in the CID spectra.

Reference

- 1 W. M. Draper, D. Wijekoon, M. McKinney, P. Behniwal, S. K. Perera and C. P. Flessel, *J. Agric. Food Chem.*, 2002, **50**, 1852-1858.

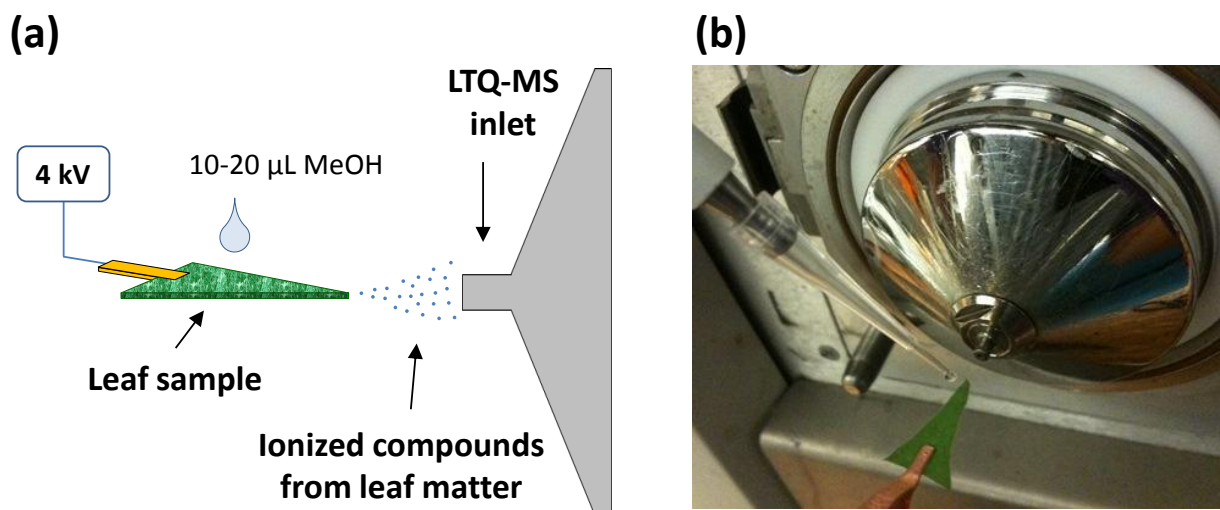


Figure S1. (a) Schematic diagram and (b) photograph of the experimental used for leaf-spray mass spectrometric detection of urushiol allergens from poison ivy plant

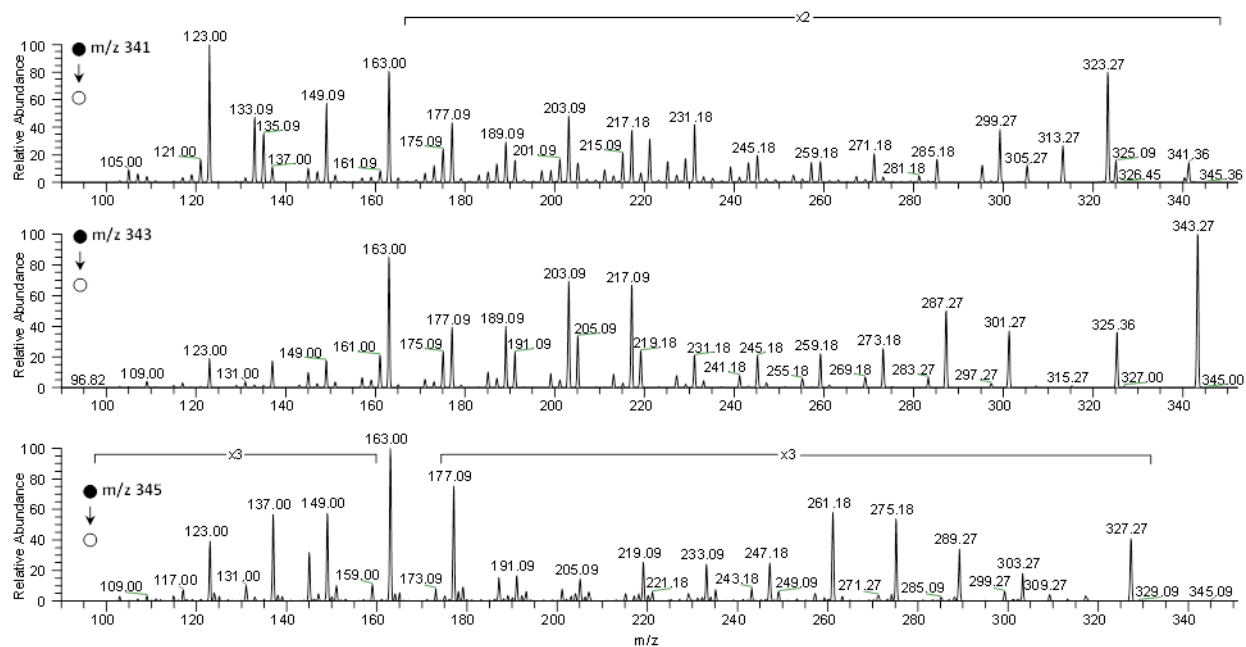
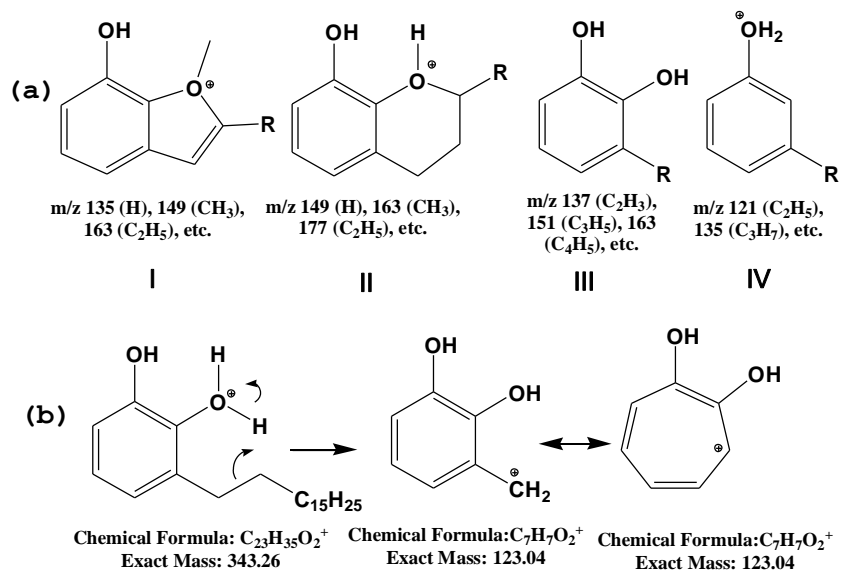


Figure S2. MS/MS spectra of three urushiols with C₁₇ side-chain obtained with leaf-spray method in positive mode. The ion being subjected to CID is indicated in the legend of each spectrum. The spray solvent was pure methanol. The fragmentation energy used for all measurements was 30 units with 1.0 Da used for the isolation of each ion in the Thermo LTQ-MS instrument.



Scheme S1. (a) The proposed structures of fragment ions of urushiols and (b) formation of the most prominent fragment ion at m/z 123 observed in all CID measurements of urushiols in positive ion mode