Electronic Supplementary Information (ESI)

Identification of oxidation products of solanesol produced during air sampling for tobacco smoke by electrospray mass spectrometry and HPLC

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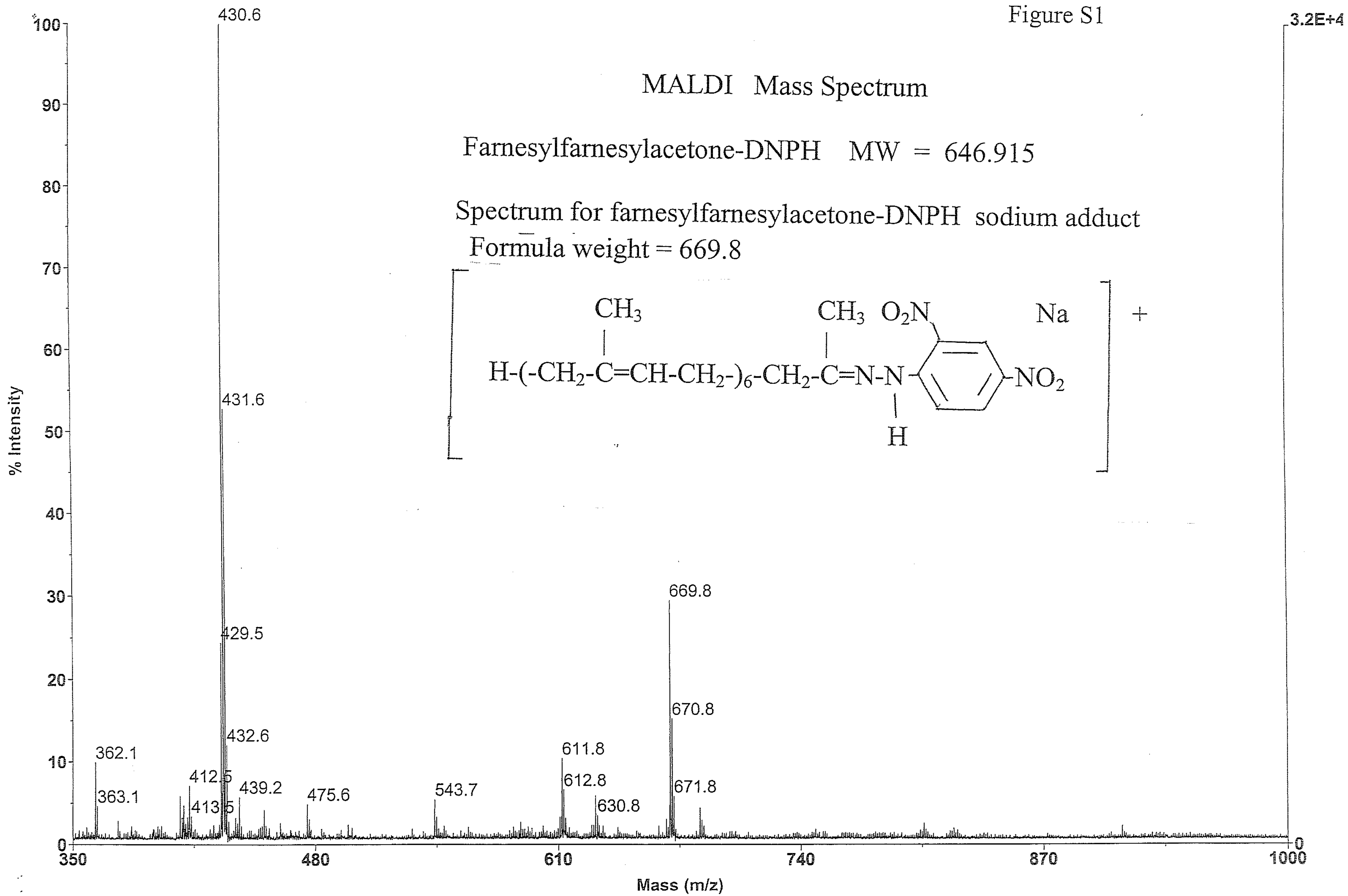
Ozone Generation System for Controlled Atmospheres. The basic operation of the system was generation of ozone at several ppm by an ozone generator inside a polyethylene bag inflated with high purity air, periodic transfer of 50-500 mL of the ozone atmosphere via a pump at ca. 250 mL/min to a plexiglass chamber where the atmosphere was diluted with incoming purified air at 6 L/min. The ozone generator was a Model XT-240 from Air-Zone, Inc., Suffolk, VA, and was designed to produce ozone without nitrogen oxides. The dimensions of the plexiglass chamber were 33 x 33 x 156 cm (w x l x h). The bursts of ozone atmosphere entered the chamber from the top; dilution air entered the chamber at 6 L/min through a port 15 cm from the top. The humidity of the dilution air was regulated by passing a fraction or all of the dilution air through a 75-L carboy filled with deionized water. A large block of flexible polyurethane foam, 31 x 31 x 5 cm, was located at the bottom of the chamber through which the diluted atmosphere exited into an exhaust tube (PVC, 8 cm O.D., followed by Tygon, 4 cm O.D.) which led to a fume hood. Sampling ports were located on all four sides of chamber at a level of 8 cm above the block of polyurethane foam. A small electric fan circulated air within the chamber. Hygrometer/thermometers (certified, traceable, Fisher Scientific) rested on the polyurethane foam.

Loading Membrane Filters with Tobacco Smoke. The tobacco smoke chamber consisted of a 26-L metal chamber (steel bucket) with a sealed lid. A 3.8-cm hole was in the lid through which filter cassettes and a lit Marlboro cigarette could be placed. The chamber was allowed to fill with tobacco smoke before filter cassettes were placed into the chamber. Eight 37-mm cassettes were placed into the chamber, and air was drawn at 1.7 L/min through the cassettes for 1 to 15 seconds (quartz membrane filters in the cassettes previously had been baked at 800 ^{o}C for 2 hrs. to remove organic contaminants). The purpose was to load the eight filters equally with tobacco smoke. However, in reality, there was some variation in the loadings.

Voyager Spec #1=>SM5[BP = 430.5, 31970]

Figure S1



M-Scan#76019 892
D:\...\5325.dat
Acquired: 16:14:00, January 22, 2004

Figure S2: ES-MS scan for APE derivatives of oxidation products of solanesol in methanol, produced by bubbling with ozone-fortified air (see text). Note that spectrum as shown is truncated for clarity; in the full display, ion at m/z 234 is most intense signal with relative abundance 100. See Figure S3 for expanded sections of this scan with more extensive labeling of relevant ions.

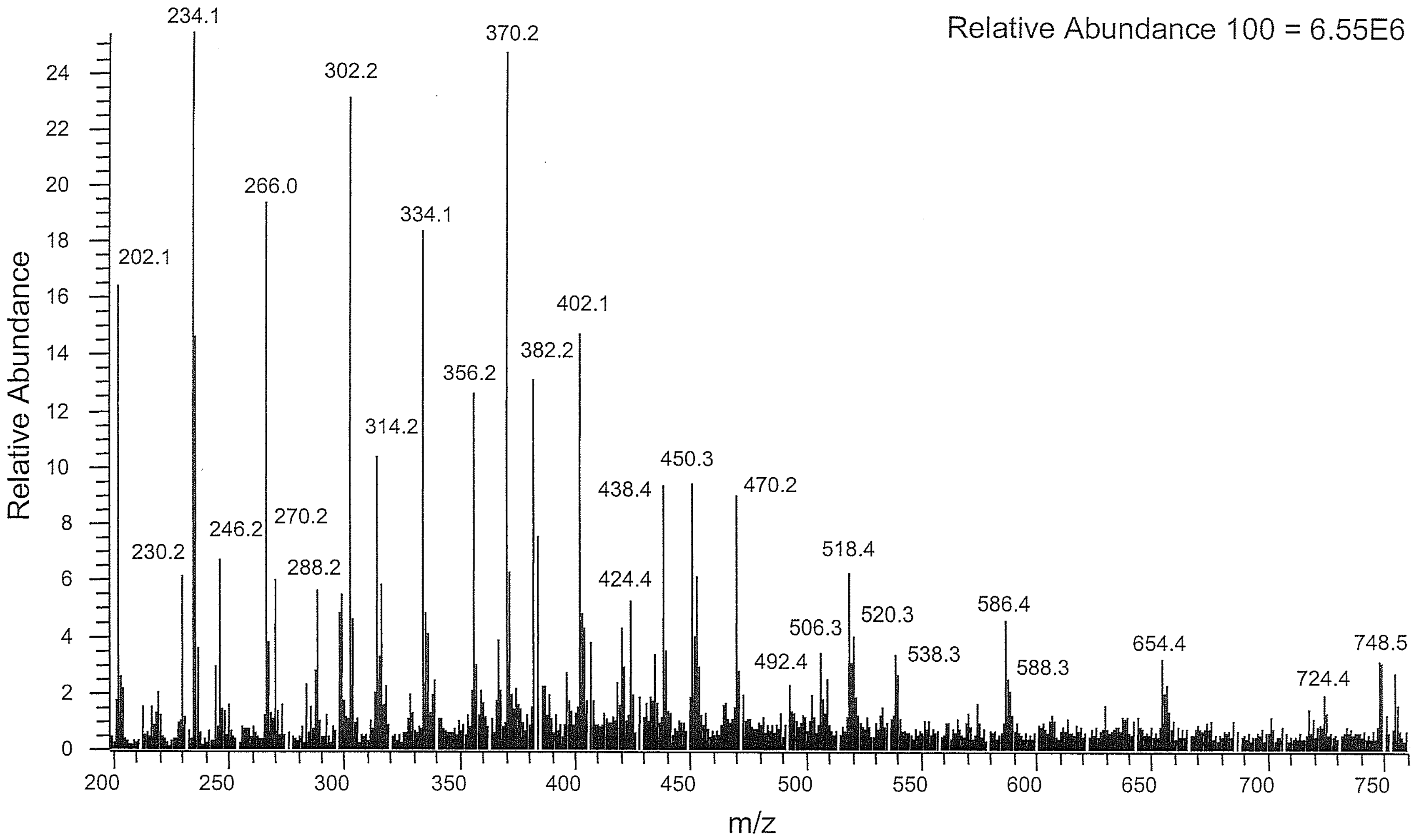


Figure S3: Closeup mass spectra from Figure S2 showing APE derivatives of solanesol ozonation products produced by bubbling in methanol solution. Boldface indicates ions identified as members of repeating series. See Table S1 for further information.

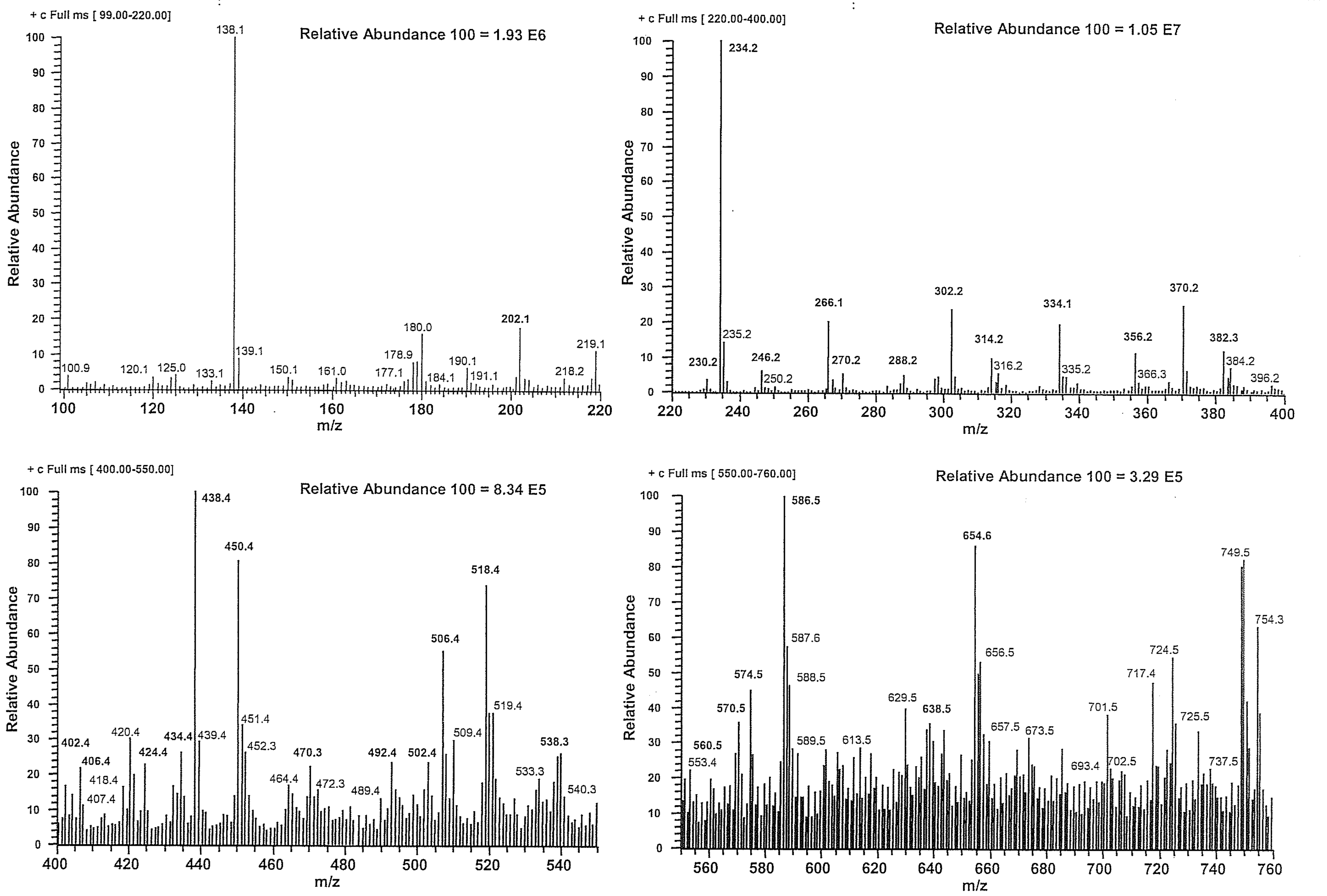


Figure S4: ES-MS spectra for aminophenylethanol derivatives of solanesol oxidation products obtained by drawing environmental air through solanesol-fortified quartz filters. See text for experimental details. Note: the relative abundance scale is truncated to allow lower intensity ions to be seen. In the full scale display, the ion at m/z 748.5 has intensity equal to relative abundance 100.

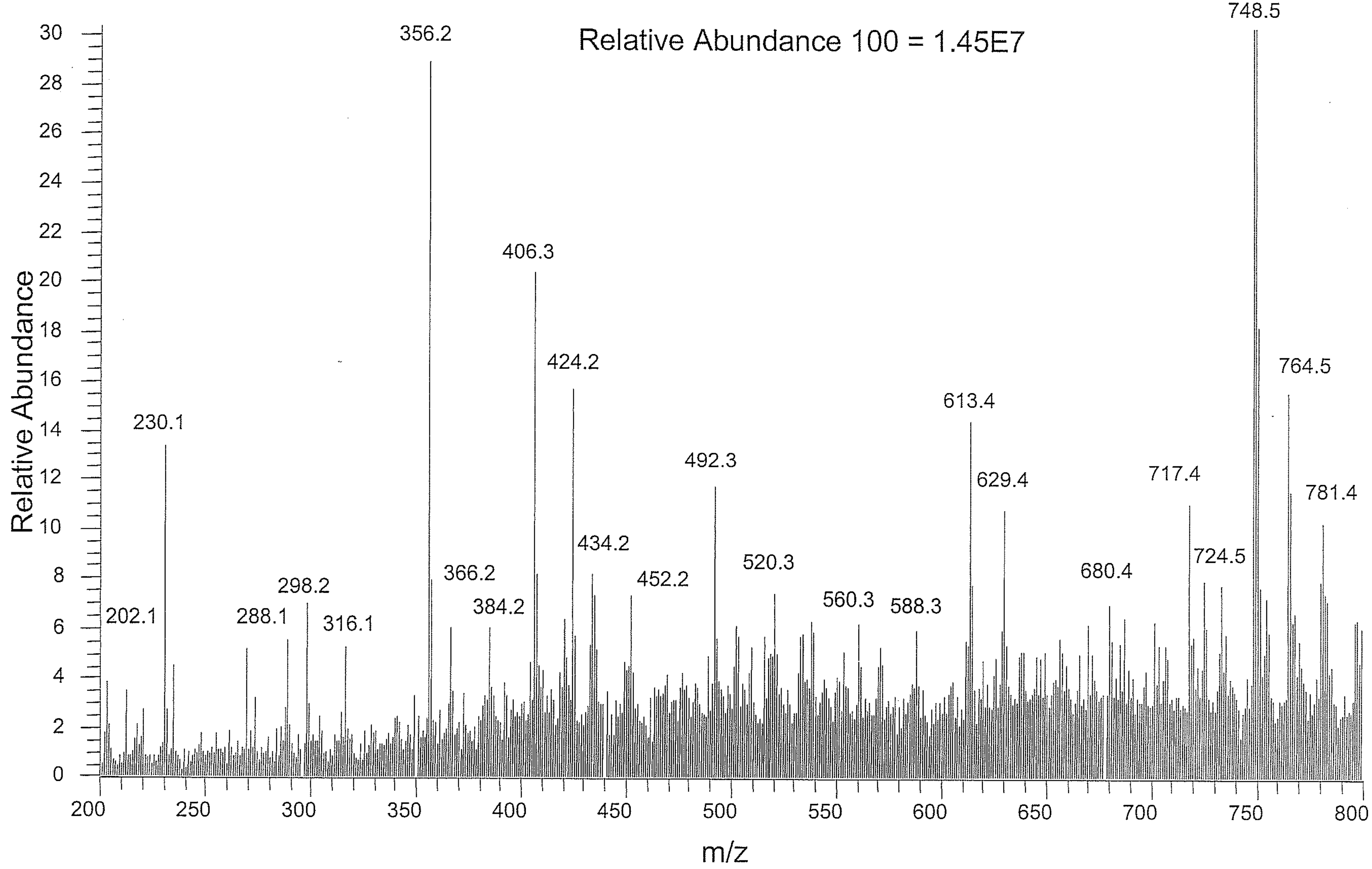


Figure S5: ES-MS scan of aminophenylethanol derivatives of solanesol oxidation products obtained by drawing high-ozone level air through quartz filters. See text for experimental details.

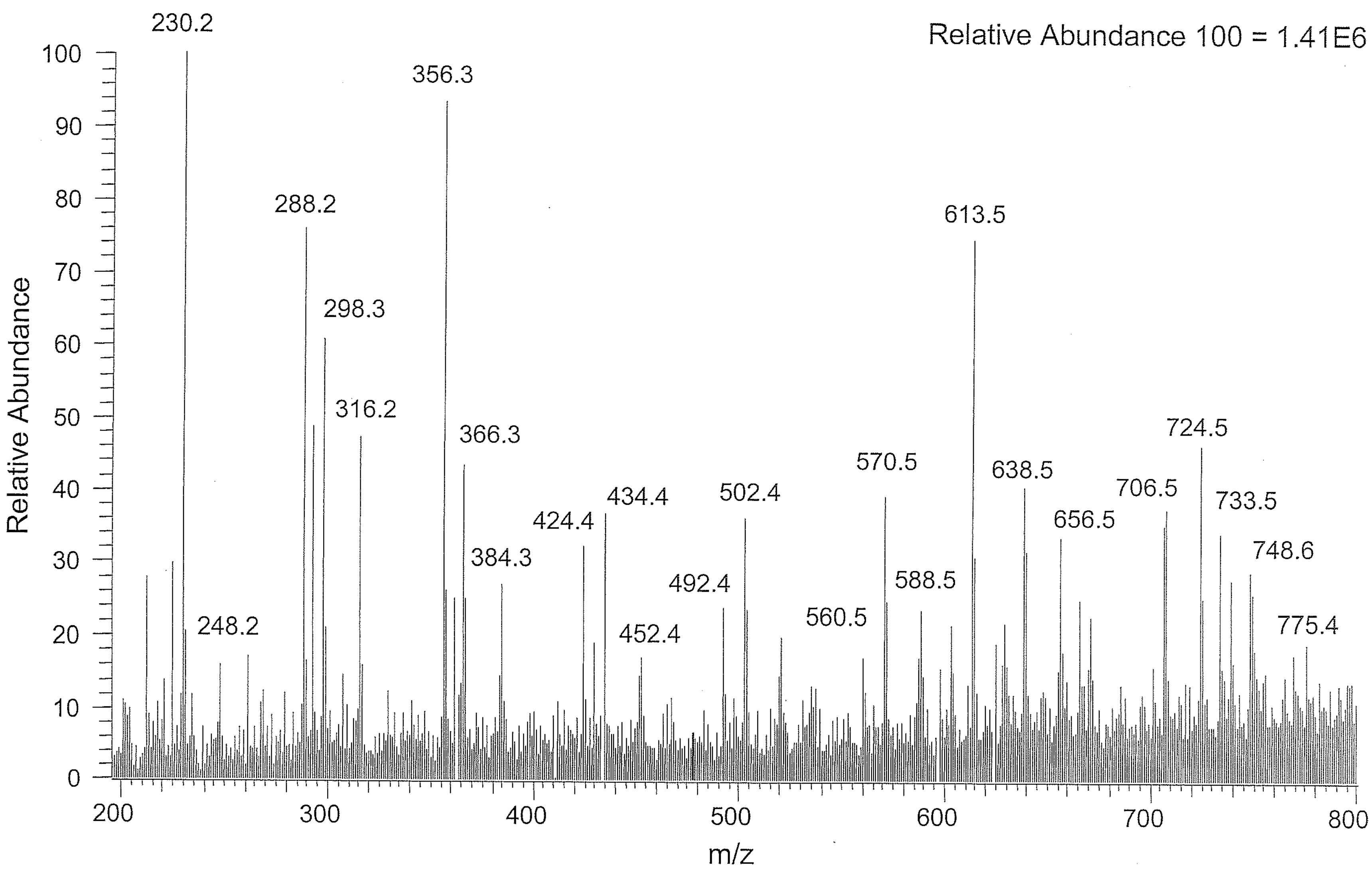


Table S1: The solanesol ozonation product ions, observed in ES-MS as their APE derivatives (Fig. S2), seem to fall into seven series. Within each series, separation by 68 m/z units (isoprene moiety) is evident. Each series has certain characteristic fragmentation patterns as listed. Where the APE derivative series correspond to those included in Scheme 1 of the main text, this is noted.

The proposed assignments for series III - VII reflect what appears to happen to the solanesol on ozonation in a bubbler filled with methanol. The isoprenoid acetones (III) do not undergo further reaction as far as we know. The isoprenoid oxoaldehydes (VI) apparently undergo addition of methanol to yield dimethyl acetal by-products, which can lose a molecule of methanol to give a second by-product (an enol ether). The latter reaction might be happening during desolvation in the ES-MS unit rather than in solution. We do not yet have proposed assignments for products that yield series I and II of APE derivatives.

I) 202, 270, 338, 406, 472	Main Fragment: Loss of 18 m/z.
II) 230, 298, 366, 434, 502, 570, 638, 706	Main Fragment: for 230 is m/z 212; for others, m/z 230. Secondary ions include loss of 18 m/z; for higher MW precursors, this is stronger than ion at 230.
III) 246, 314, 382, 450, 518, 586, 654, 722 (APE derivatives of isoprenoid acetone products) Group C in Main Text, Scheme 1.	Main Fragment m/z 190. Secondary ions include loss of 16 m/z, more prominent for precursors at higher MW.
IV) 248, 316, 384, 452, 520, 588, 656, 724 (APE derivatives of hydroxyisoprenoid acetaldehydes) Group D in Main Text, Scheme 1.	Main Fragment: Loss of 18 m/z.
VI) 266, 334, 402, 470, 538 (APE derivatives of dimethyl acetal by-products of isoprenoid oxoaldehydes) Group F in Main Text, Scheme 1.	Main Fragment: Loss of 32 m/z. Fragment spectra tend to be simple.
V) 288, 356, 424, 492, 560, 628 (APE derivatives of isoprenoid oxoaldehyde products) Group G in Main Text, Scheme 1.	Main Fragment: m/z 230. Secondary ions include loss of 18 m/z
VII) 234, 302, 370, 438, 506, 574, 642 (APE derivatives of dimethyl acetal by-products of isoprenoid oxoaldehydes with loss of methanol) See Main Text Figure 5 for structure prior to derivatization.	Main Fragment: Loss of 32 m/z. Important secondary ions include 190 and 232.