

Photochemical and oxidative degradation of chamazulene contained in *Artemisia*, *Matricaria* and *Achillea* essential oils and setup of protection strategies

Simone Gabbanini,^{*1} Jerome Ngwa Neba,² Riccardo Matera,¹ Luca Valgimigli, ^{*2,3}

¹ R&D Department, BeC s.r.l., Via C. Monteverdi 49, 47122 Forlì, Italy; laboratorio@bec-natura.com

²Department of Chemistry "Ciamician", University of Bologna, Via Gobetti 85, 40129 Bologna, Italy; luca.valgimigli@unibo.it

³ Tecnopolo di Rimini, Via D. Campana 71, 47922 Rimini, Italy.

APPENDIX (Supplementary data)

Table of Contents

Figure S1. GC-MS analysis of <i>A. arborescens</i> , <i>M. chamomilla</i> and <i>A. millefolium</i> EOs.	Page 2
Figure S2. Spectral radiation power distribution of Ultra-Vitalux lamp	Page 2
Figure S3. Fragmentation of parent peak <i>m/z</i> 215, calculated by Mass Frontier software	Page 3
Figure S4. GC-MS calibration curve of CA in Total Ion Count (TIC) mode	Page 4
Figure S5. LC-PDA calibration curve of CA at 349 nm	Page 4
Figure S6. Example of LC-PDA chromatograms of mixtures of CA and antioxidants.	Page 5
Figure S7. Example of LC-PDA chromatograms of mixtures of CA (0.17 mM) with UV filters	Page 6
Figure S8. Spectrophotometric evaluation of CA photodegradation in the absence of oxygen	Page 7
Figure S9. Detail of chamazulene degradation with selected antioxidants, incubated at 50°C.	Page 7

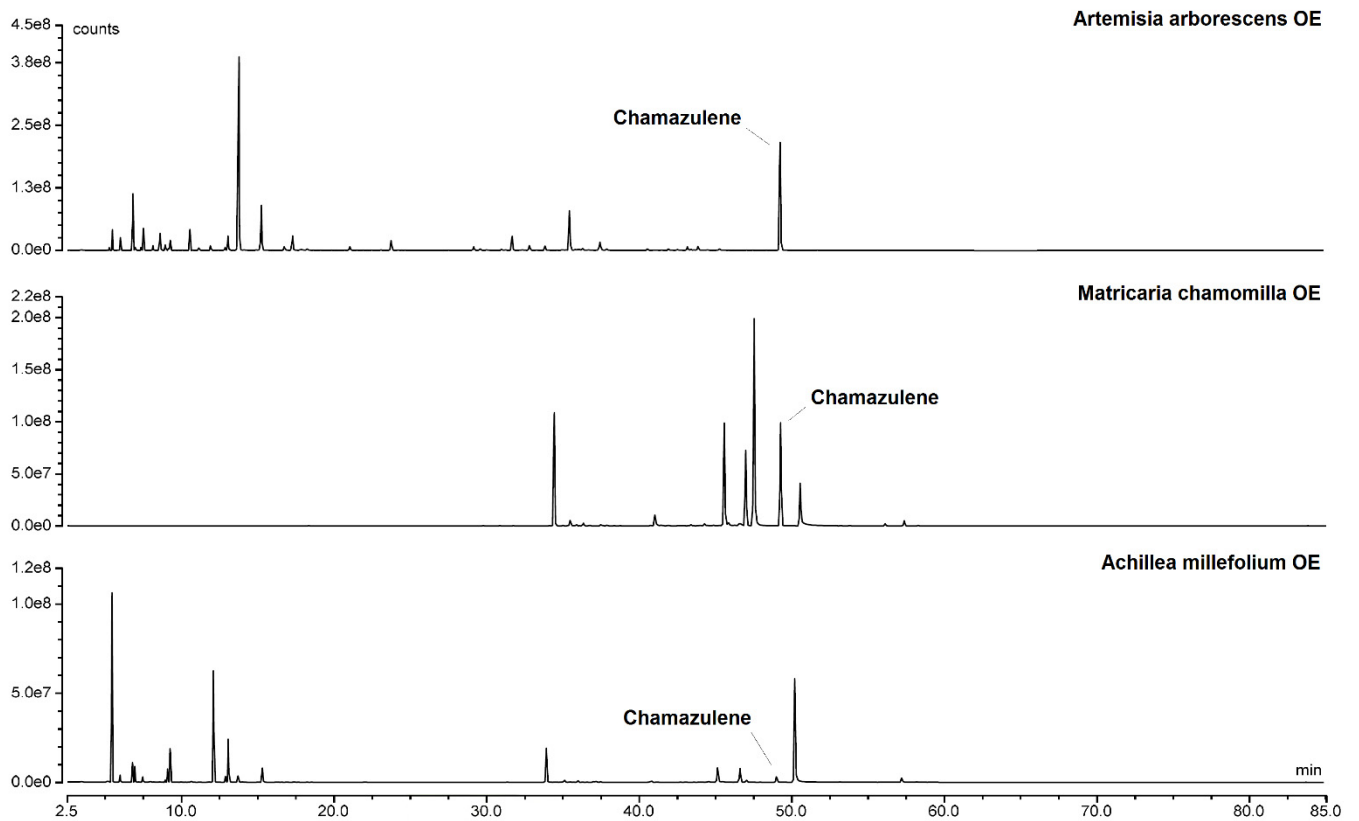


Figure S1. GC-MS analysis of three representative EO samples of *A. arborescens*, *M. chamomilla* and *A. millefolium*, comparatively screened to identify the most convenient source of chamazulene for isolation. The respective chamazulene content was 13.6%, 9.6% and 1.2% by peak area in TIC chromatograms.

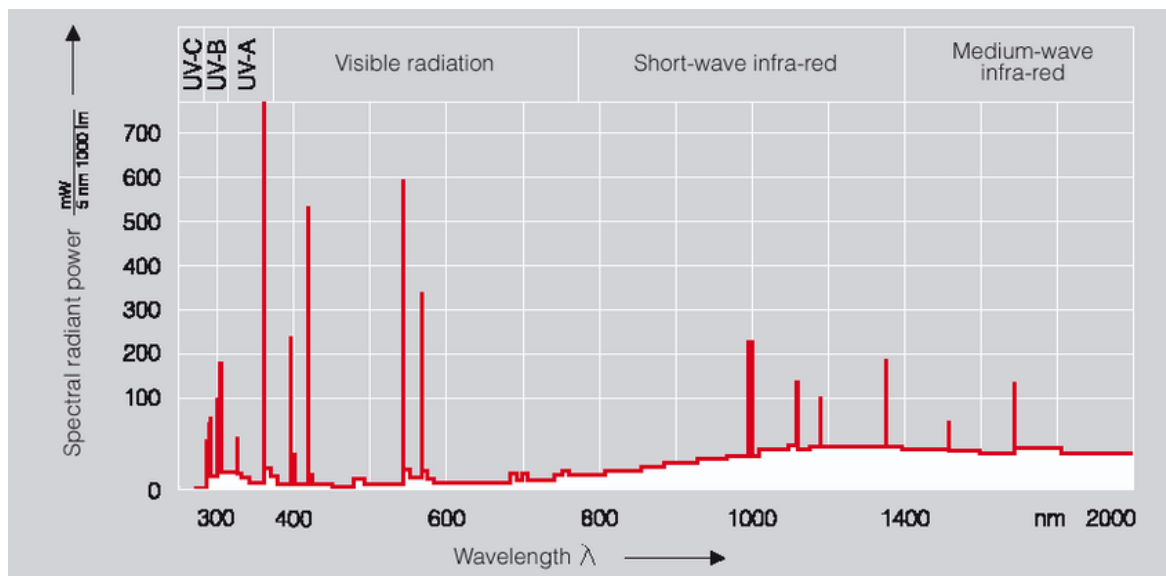


Figure S2. Spectral radiation power distribution of Osram Ultra-Vitalux® lamp at various wavelengths. Data provided by the lamp manufacturer, reported only as a reference.

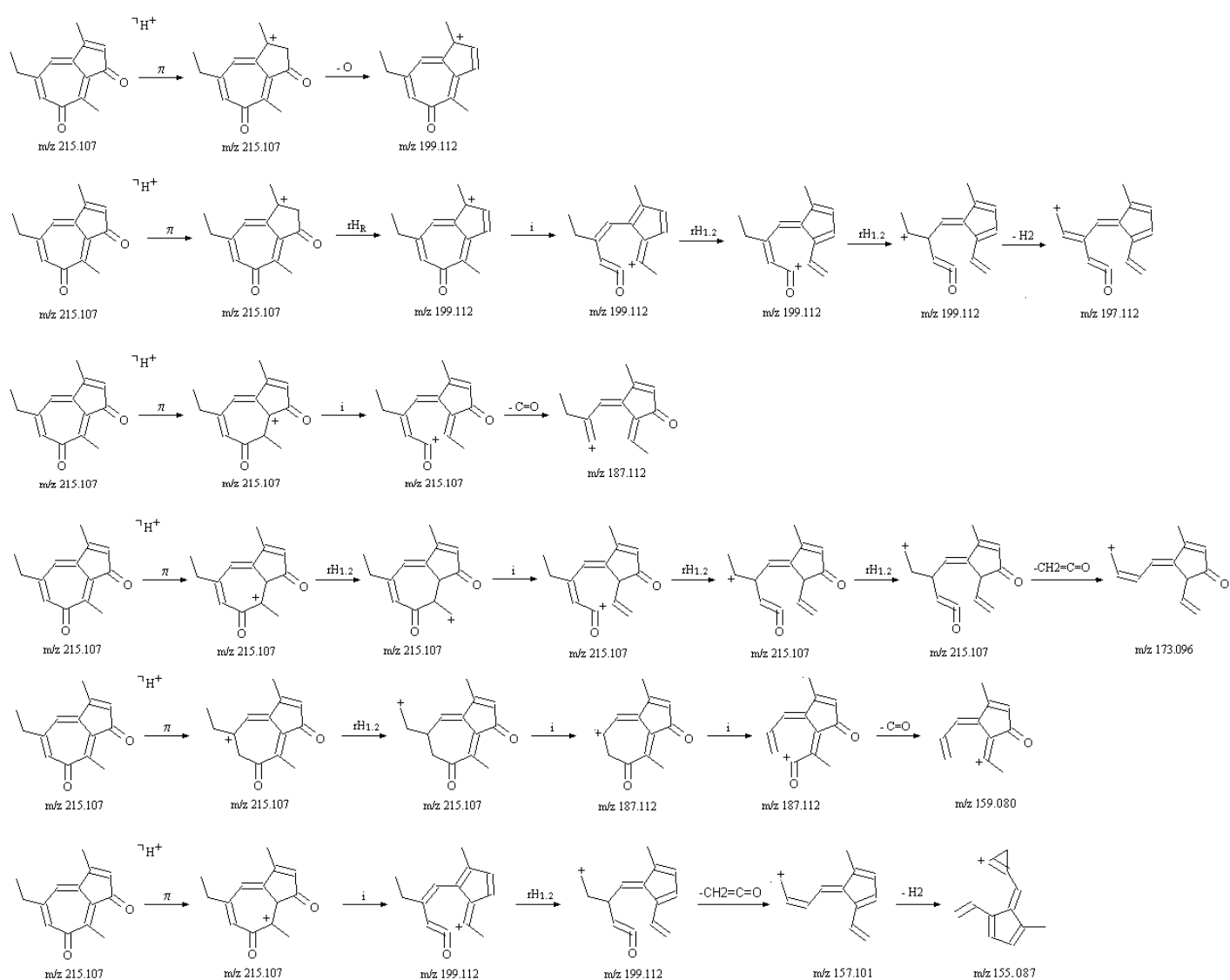


Figure S3. Fragmentation ions of parent peak m/z 215, in positive mode attributed to chamazulene quinone (6), calculated by Mass Frontier software. The fragmentation pattern explains ions with m/z 197, 187 and 159 shown in Figure 9.

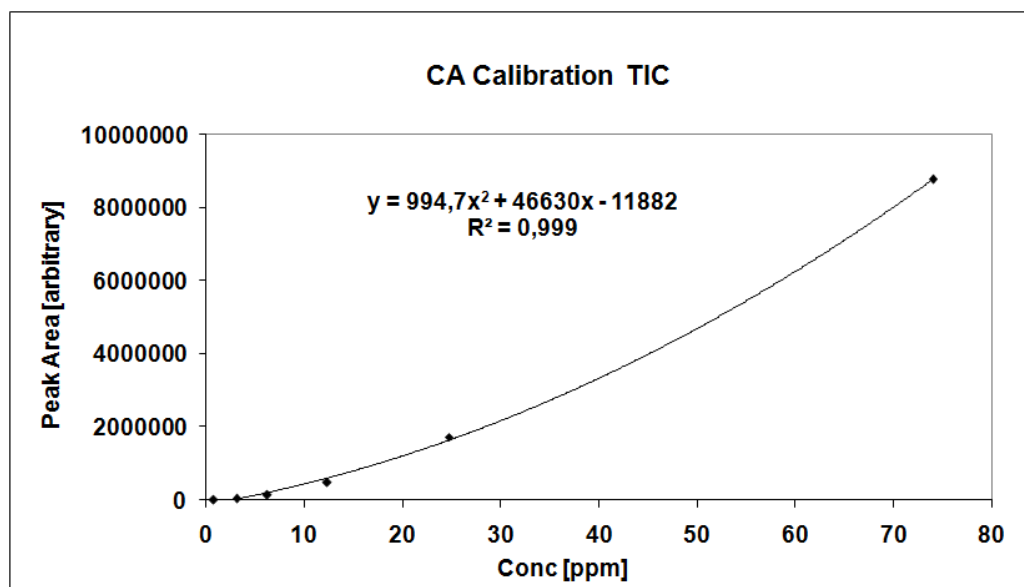


Figure S4. GC-MS calibration curve of CA in Total Ion Count (TIC) mode, used to evaluate the influence of solvent type and presence of oxygen on the photostability of CA alone.

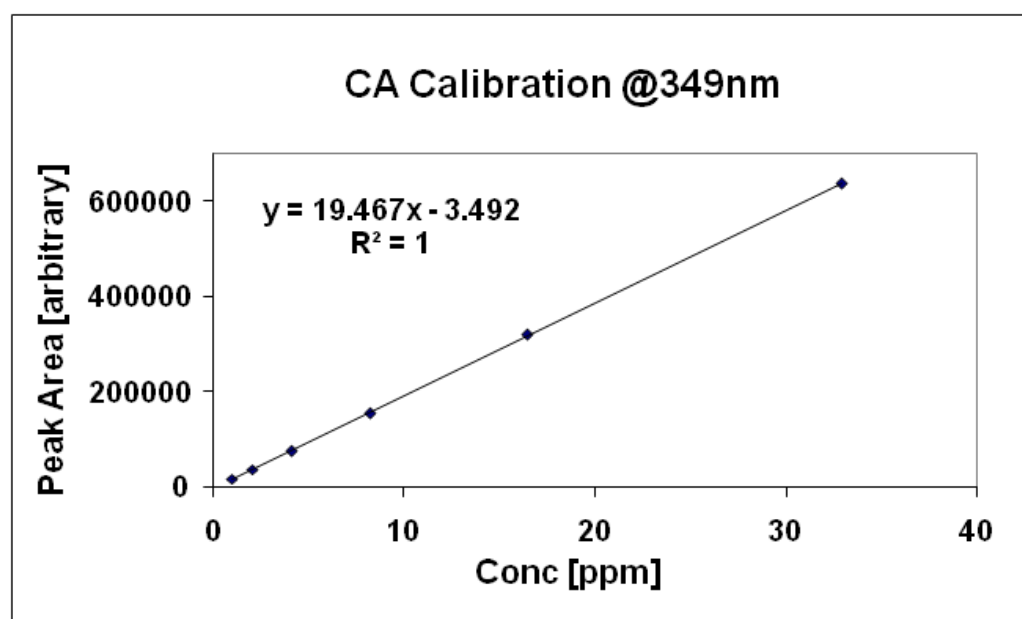


Figure S5. LC-PDA calibration curve of CA at 349 nm used for evaluation of photo and thermal stability experiments of CA in presence of antioxidants and sunscreens.

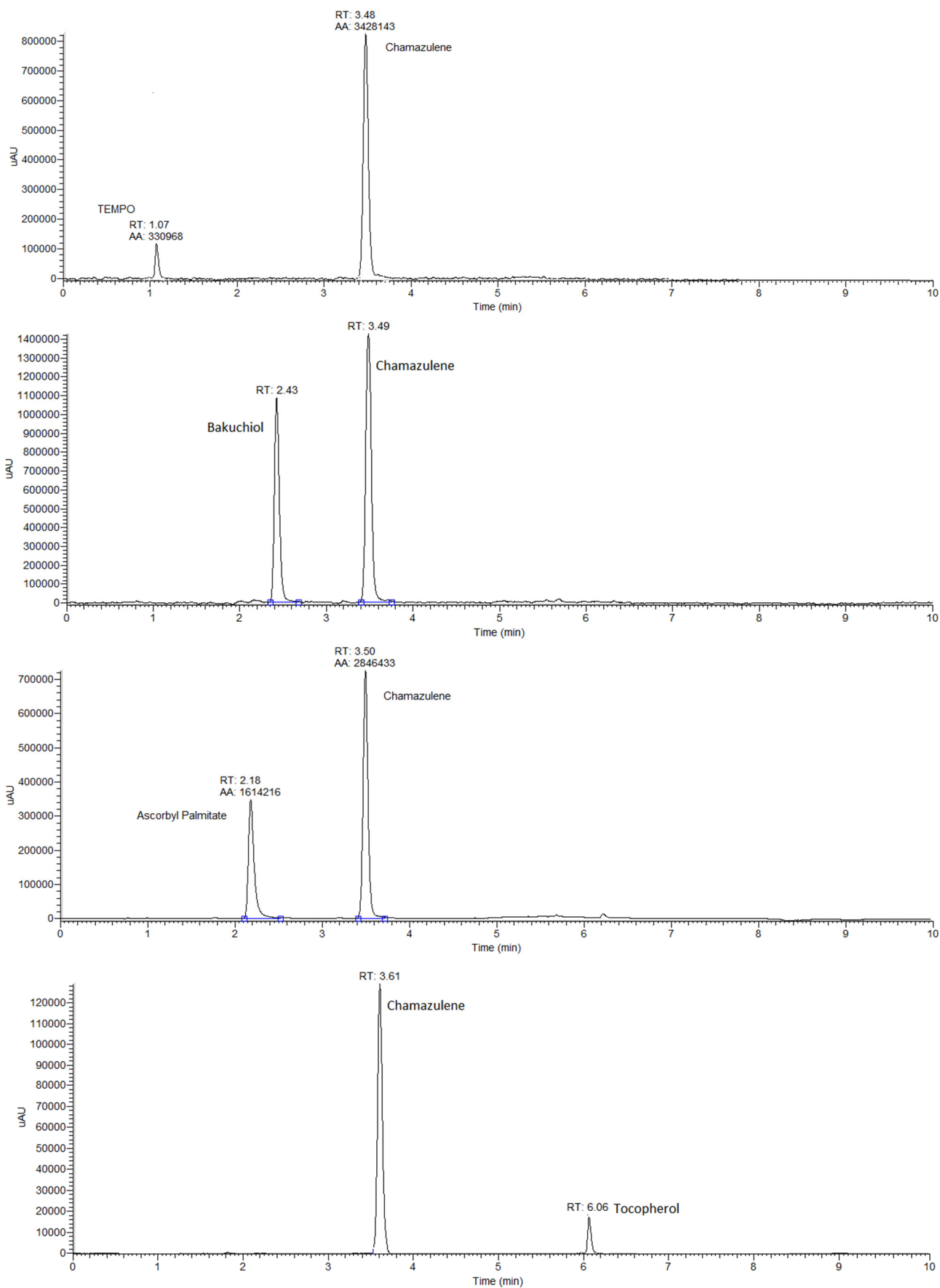


Figure S6. Example of HPLC-PDA chromatograms of mixtures of CA:antioxidants in molar ratio 1:10. From top to bottom: TEMPO, bakuchiol, ascorbyl palmitate, tocopherol.

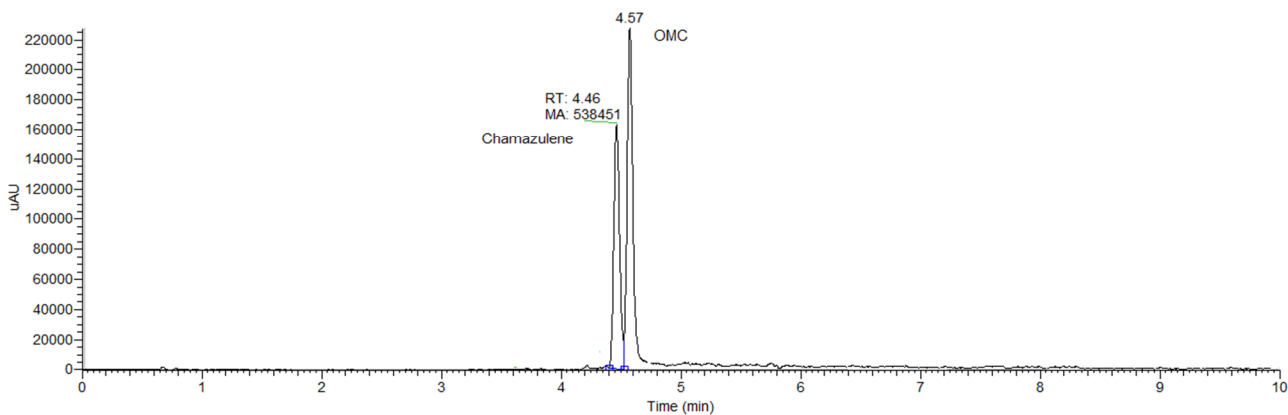
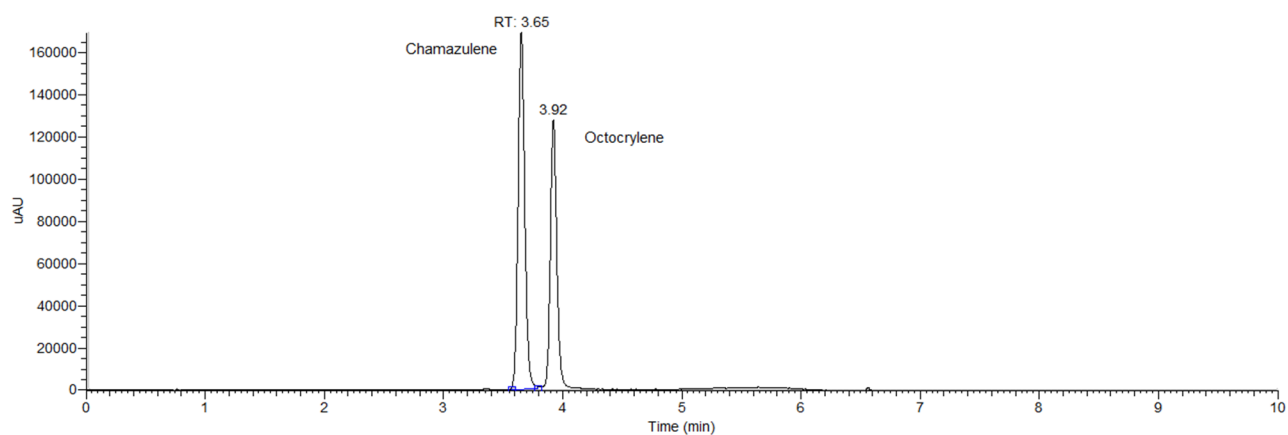
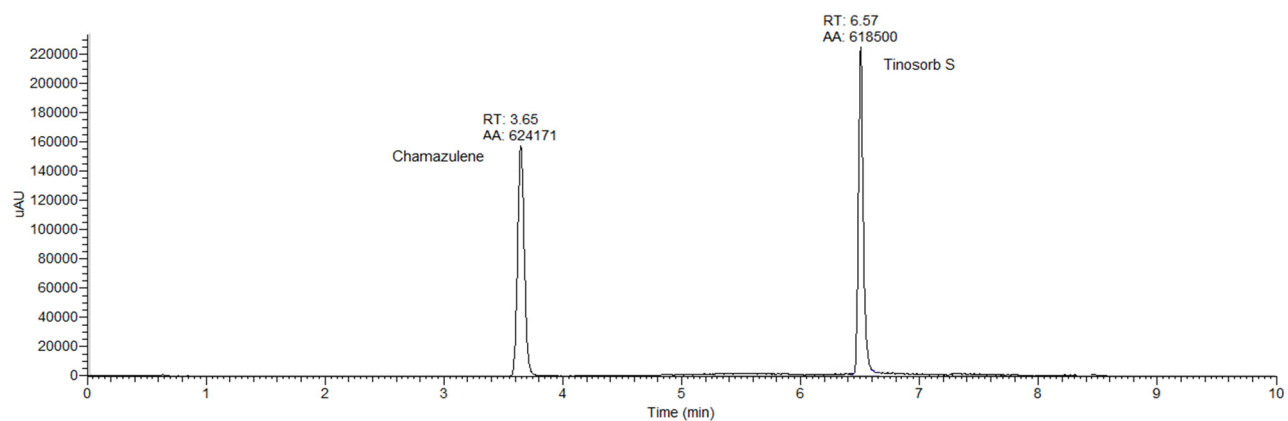


Figure S7. Example of LC-PDA chromatograms of mixtures of CA (0.17 mM) with UV filters at a concentration of 5% w/v (from top to bottom: Tinosorb® S, octocrylene, octyl methoxycinnamate). The chromatographic conditions were slightly changed for octyl methoxycinnamate to resolve coelution with chamazulene..

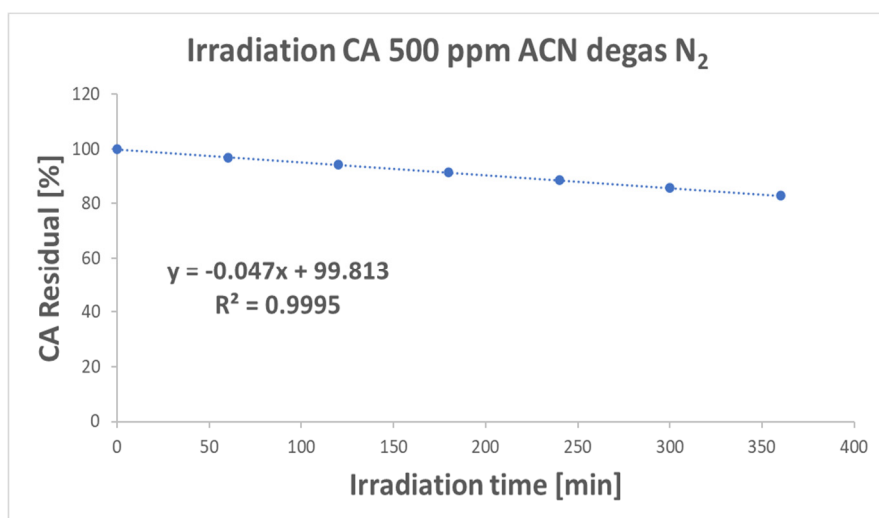


Figure S8. Spectrophotometric evaluation of CA photodegradation in the absence of oxygen. Measurements were performed in a sample of CA 500 ppm in acetonitrile in a 3.5 mL Teflon sealed quartz cuvette and degassed for 5 minutes with an abundant N₂ stream. The cuvette was subjected to UVA-UVB radiation at 100 mW/cm² (strong photooxidation conditions) for 6 hours. At regular time intervals a spectrophotometric reading was performed without opening the cuvette. The rate of the CA degradation is reported.

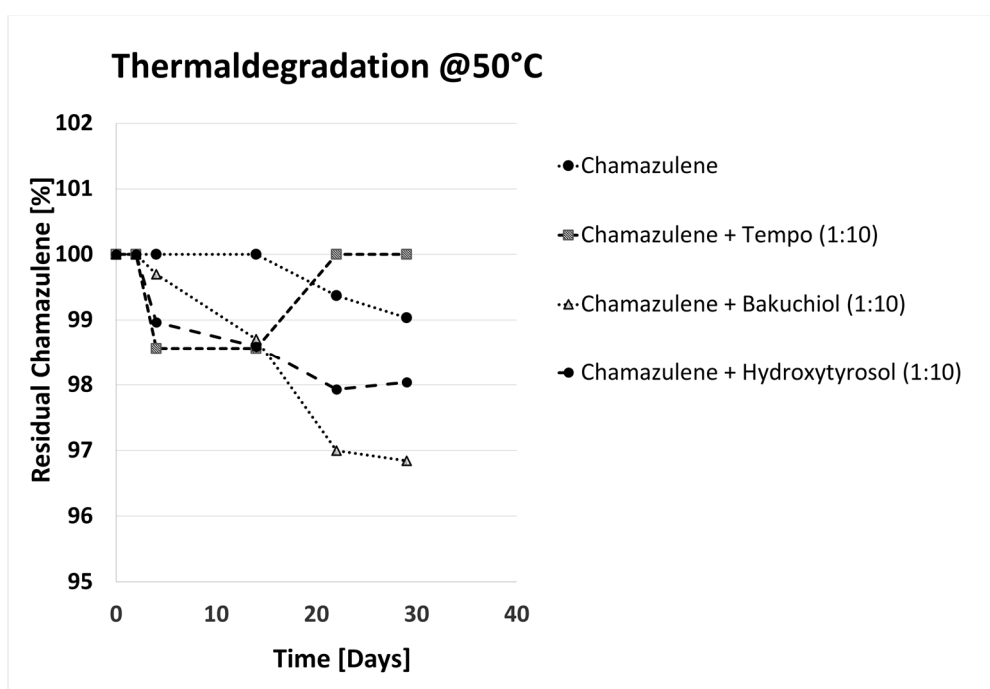


Figure S9. Detail of thermal degradation of chamazulene in solution, alone or in the presence of selected antioxidants, incubated at 50°C. This figure represents an expansion of Figure 12 in the manuscript.