

SUPPLEMENTARY MATERIAL

Mapping Degradation Pathways of Natural and Synthetic Dyes with LC-MS: Influence of Solvent on Degradation Mechanisms

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S-1 Influence of injection volume: de-mixing effects

Good peak shapes are observed when injecting small volumes, as shown in Figure S-1 (5- μ L injection). When injecting larger volumes (e.g. 20 μ L) detection limits are lowered, but peak deformation may occur, as described in the main text.

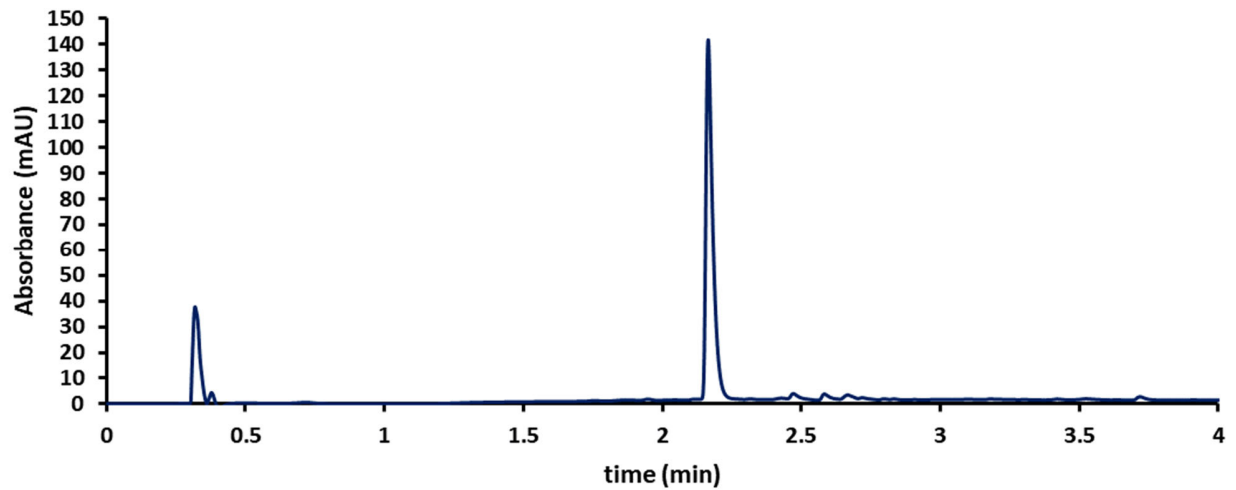
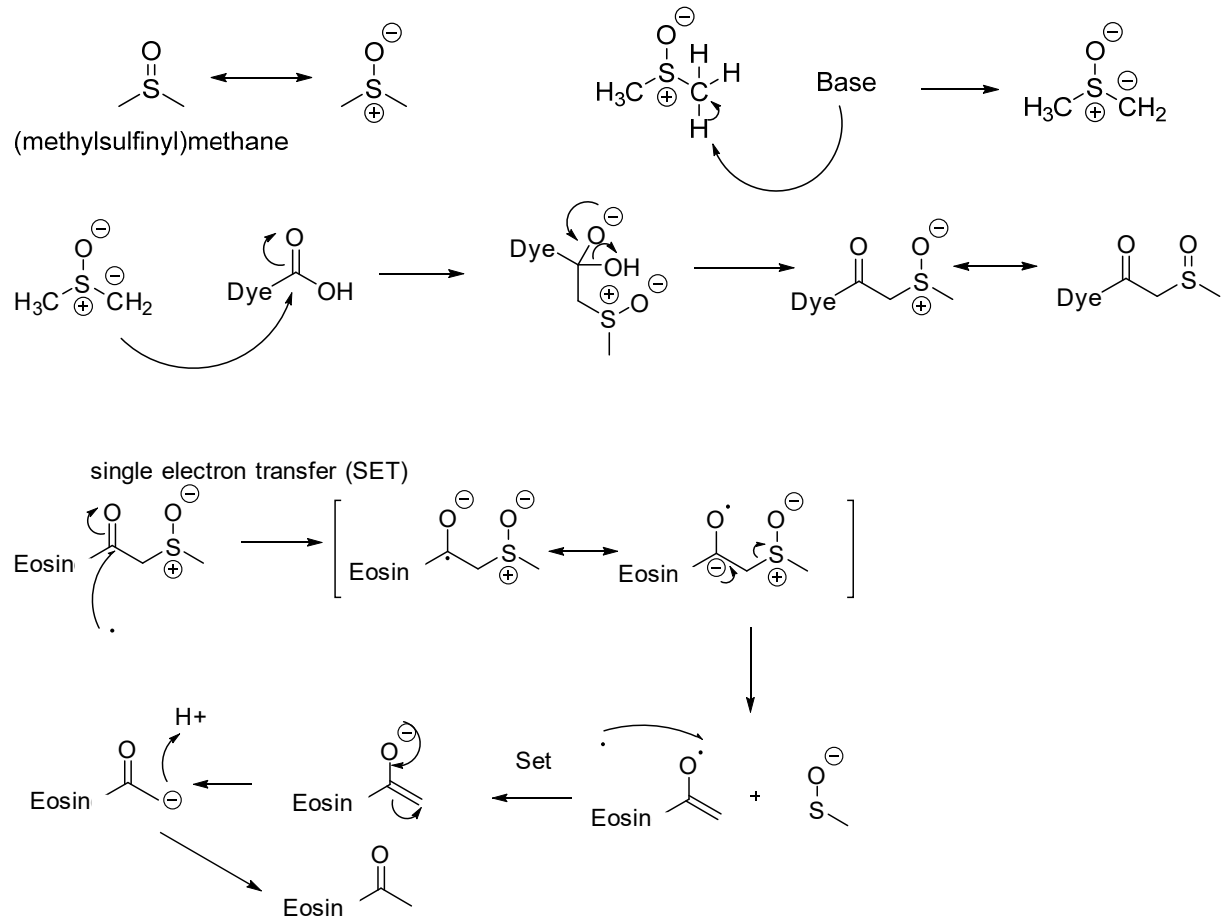


Figure S-1 – LC-UV chromatogram of the analysis of carminic acid dissolved in DMSO. Detection wavelength 254 nm. Injection volume: 5 μ L.

S-2 Interaction of DMSO with carminic acid, eosin and their degradation products

The reaction mechanism below clarifies the interaction of DMSO with the carboxylic-acid groups [1–5] of carminic acid, eosin and their degradation product. The authors acknowledge Rien Reijneveld for compiling this overview.



Reductive cleavage through single electron transfer

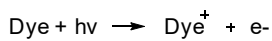


Figure S-2 – Reaction mechanism for interaction of carboxylic acid with DMSO.

S-3 MS/MS data of carminic acid with DMSO

The MS/MS spectrum shown below confirms the interaction and reaction of DMSO with carminic acid.

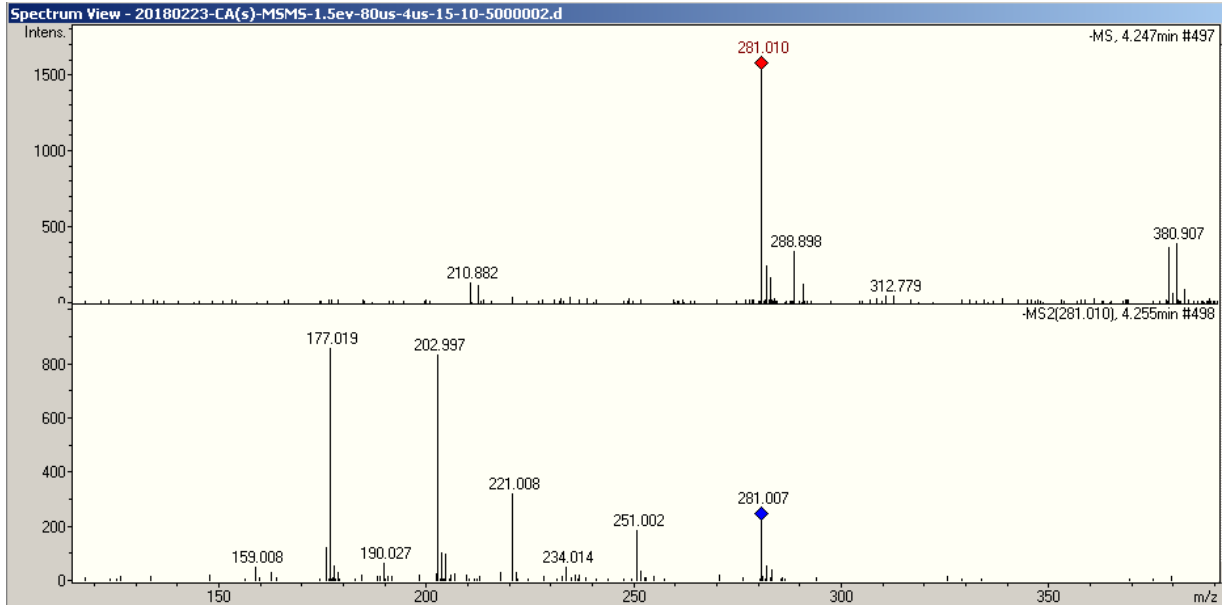


Figure S-3 – MS/MS spectrum of analyte formed (m/z 281.01) by the reaction of carminic acid (221.01) with DMSO and the subsequent removal of water (m/z differences of 60 Da).

S-4 MS/MS and UV-vis data of carminic-acid degradation product

The MS/MS spectra below display the removal of carboxylic acid from precursor ion with m/z 221.0 to product ion with m/z 177.0. As a result, it can be concluded that a carboxylic-acid moiety is present.

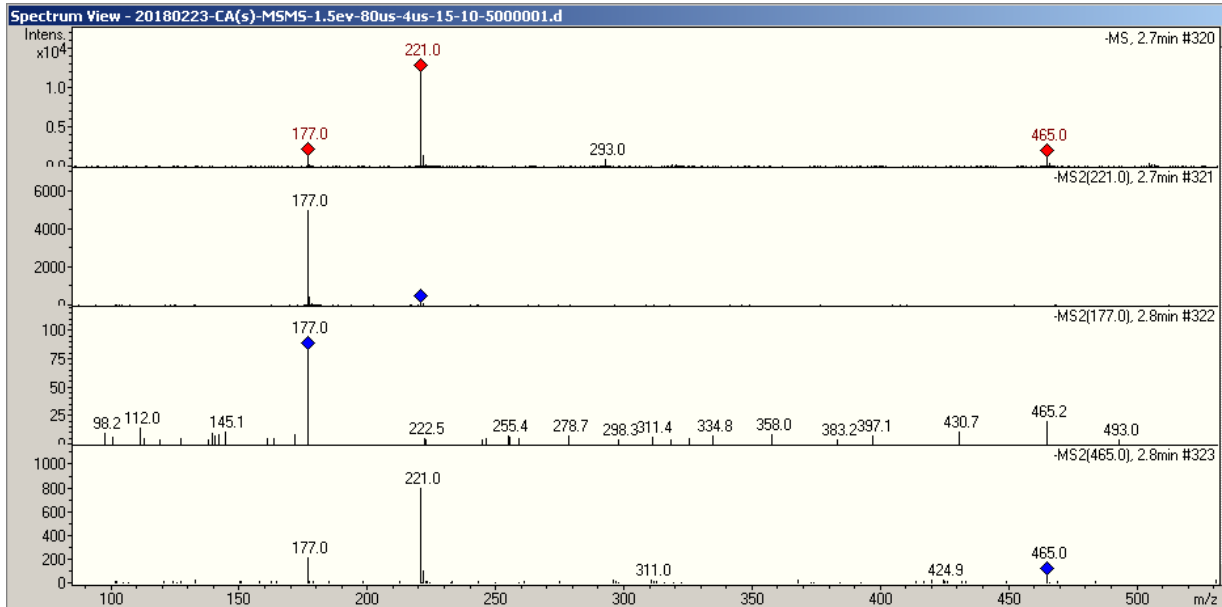


Figure S-4 - MS/MS spectra of one of the degradation products of carminic acid (m/z 221.0).

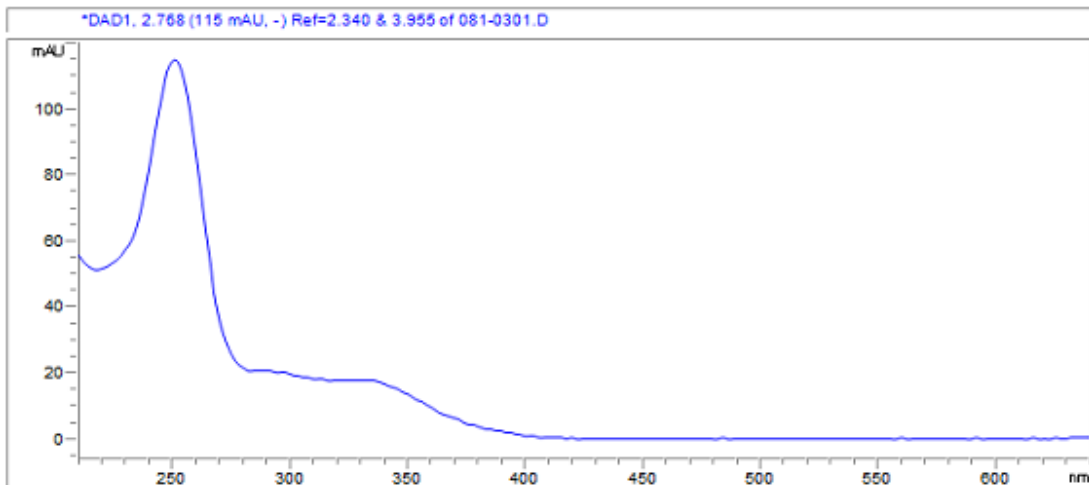


Figure S-5 – UV-vis spectrum of degradation product of carminic acid (m/z 221.0).

S-5 Loss of Bromine in Eosin

The reaction mechanism below clarifies the loss of bromine under the influence of light [6–8]. The authors acknowledge Rien Reijneveld for compiling this overview.

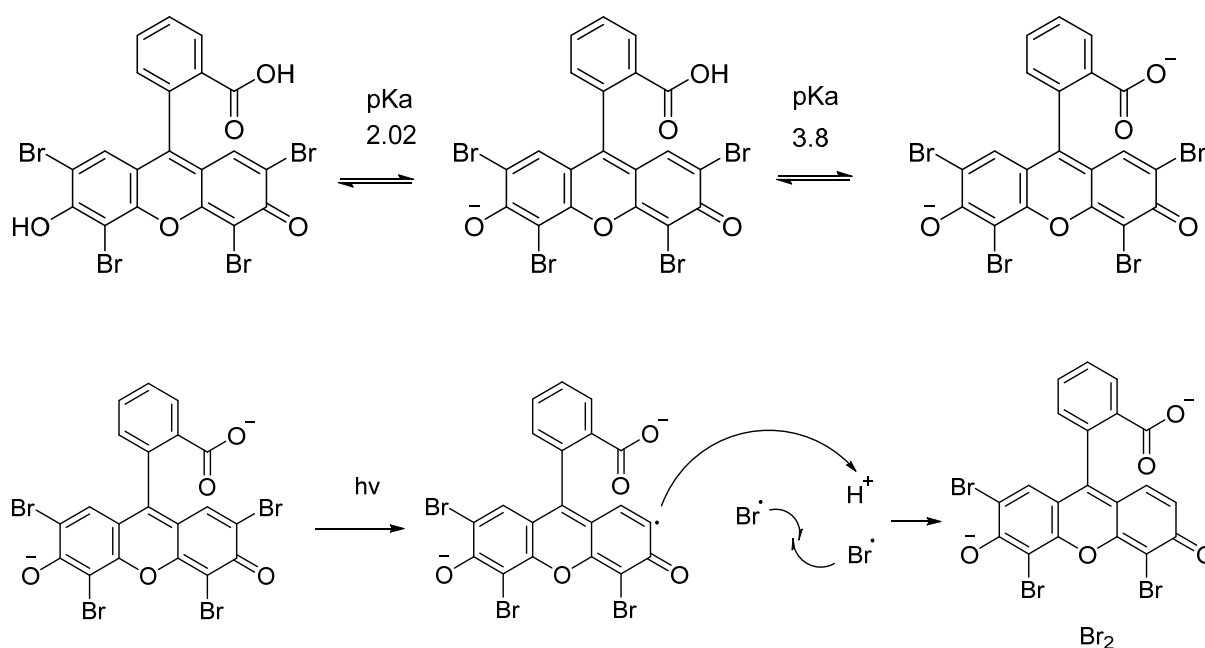


Figure S-6 – Reaction mechanism for the loss of bromine under the influence of light.

S-6 MS/MS data for eosin interaction with DMSO

The MS/MS spectrum shown below confirms the interaction of eosin with DMSO.

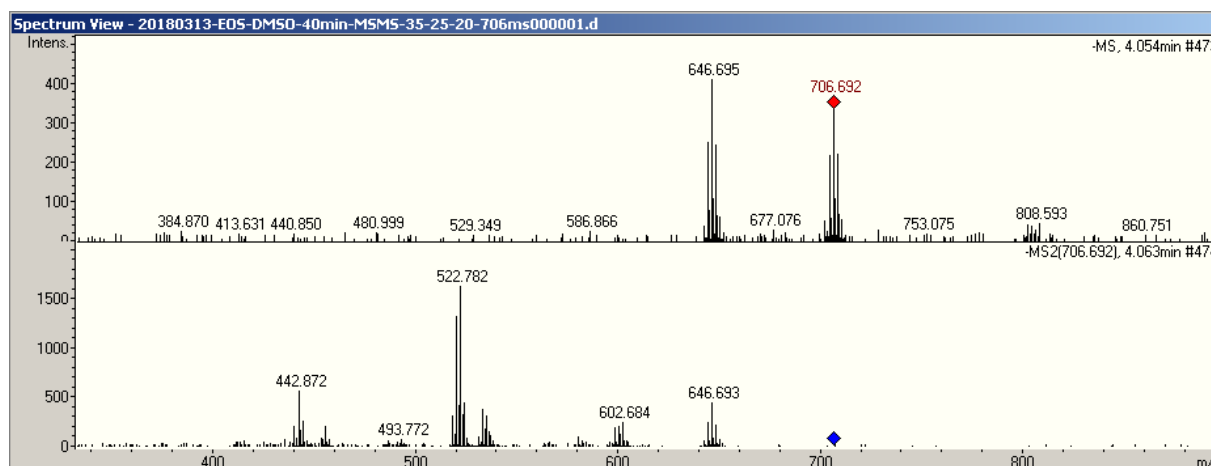


Figure S-7 – MS/MS spectra of the product (m/z 706.69) of DMSO interaction with eosin (m/z 646.69).

S-7 MS/MS and UV-vis data for eosin degradation products as a result of loss of bromine

One of the degradation pathways found for eosin was the (subsequent) loss of one (or multiple) bromine atoms. The MS/MS and UV-vis spectra below were used to tentatively identify these compounds. Information obtained from the typical isotope ratios indicating the presence of one or more bromine atoms is indispensable.

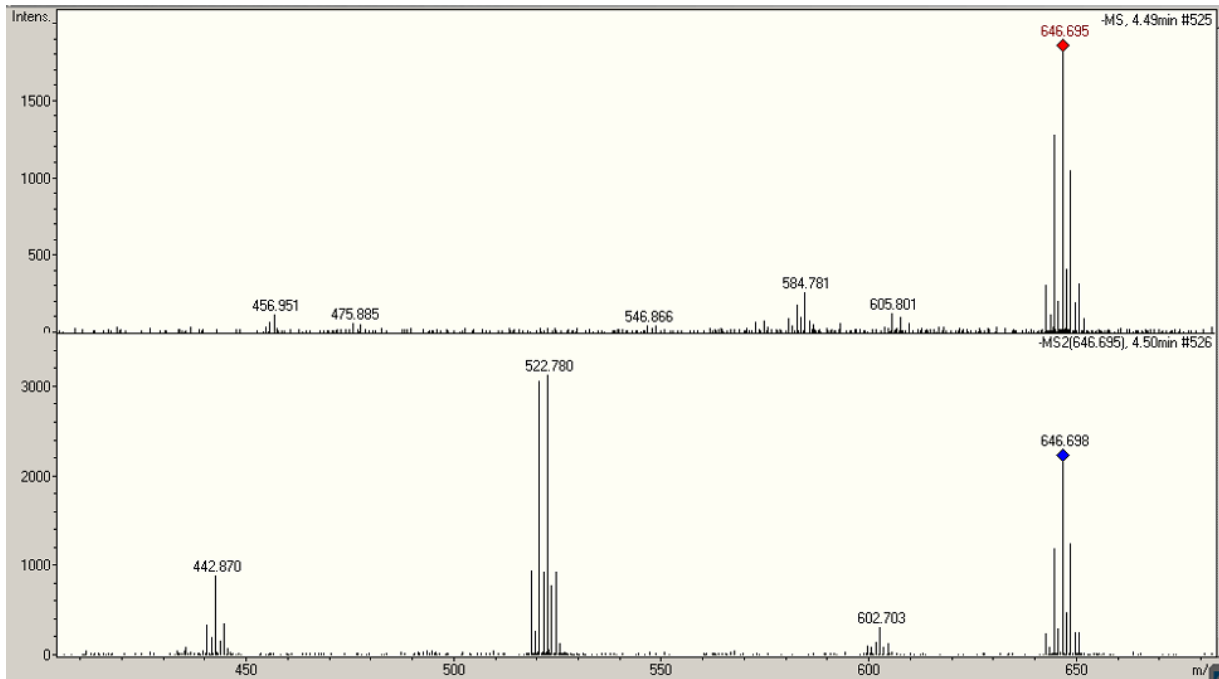


Figure S-8 - MS/MS spectra of eosin (m/z 646.69).

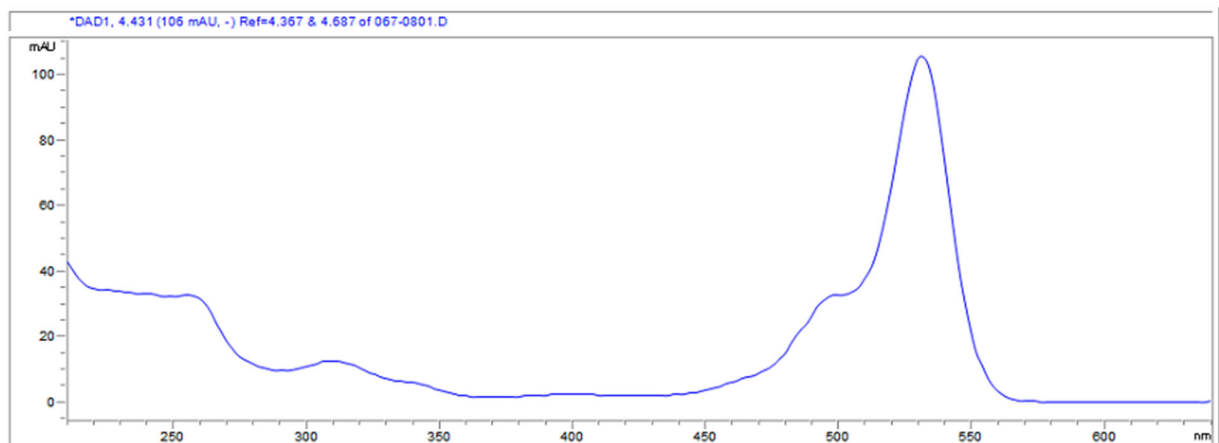


Figure S-9 – UV-vis spectrum of eosin (marked 1 in Figure 5).

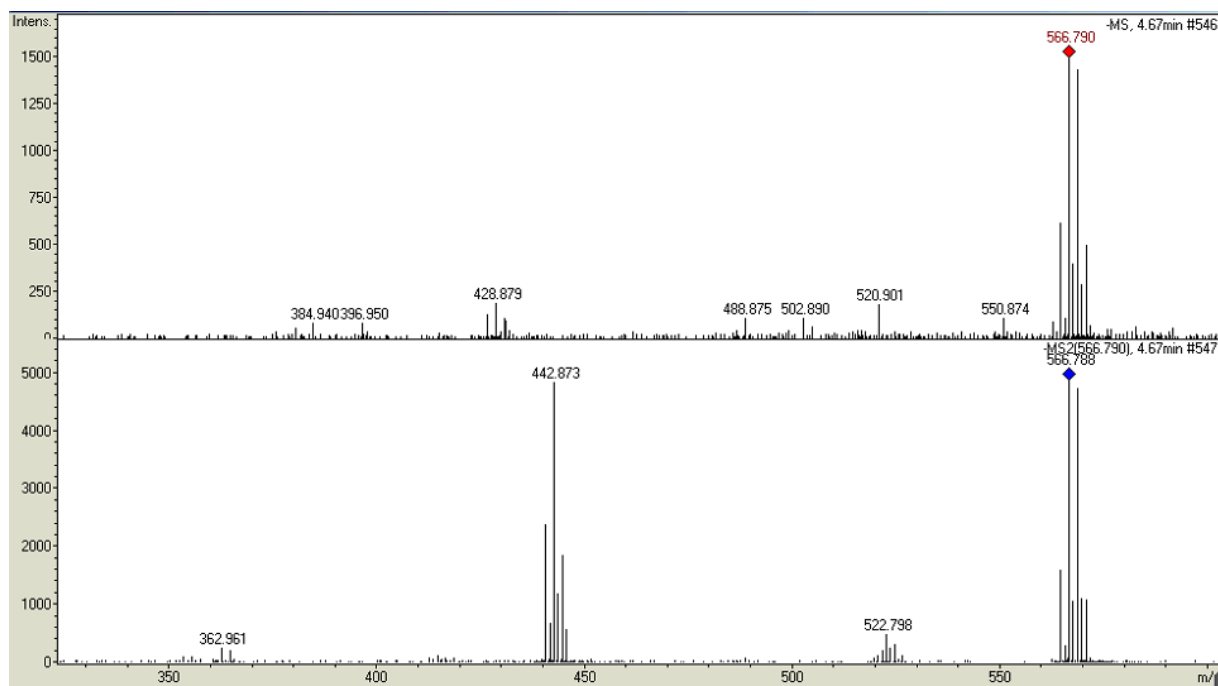


Figure S-10 - MS/MS spectra of eosin after the loss of one bromine atom (m/z 566.79).

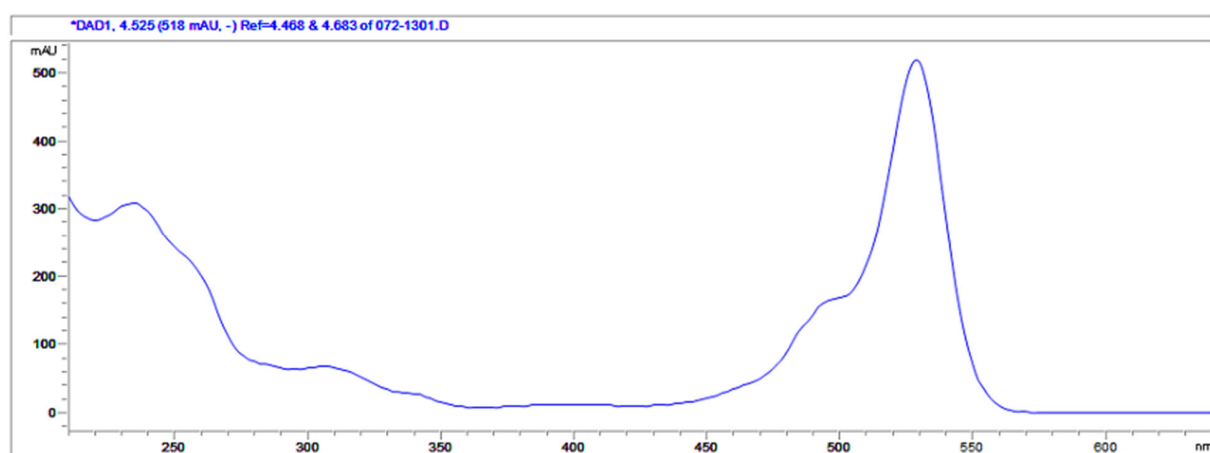


Figure S-11 – UV-vis spectrum of eosin after the loss of one bromine atom (marked 2 in Figure 5). It should be noted that the spectrum is not pure due to (partial) co-elution.

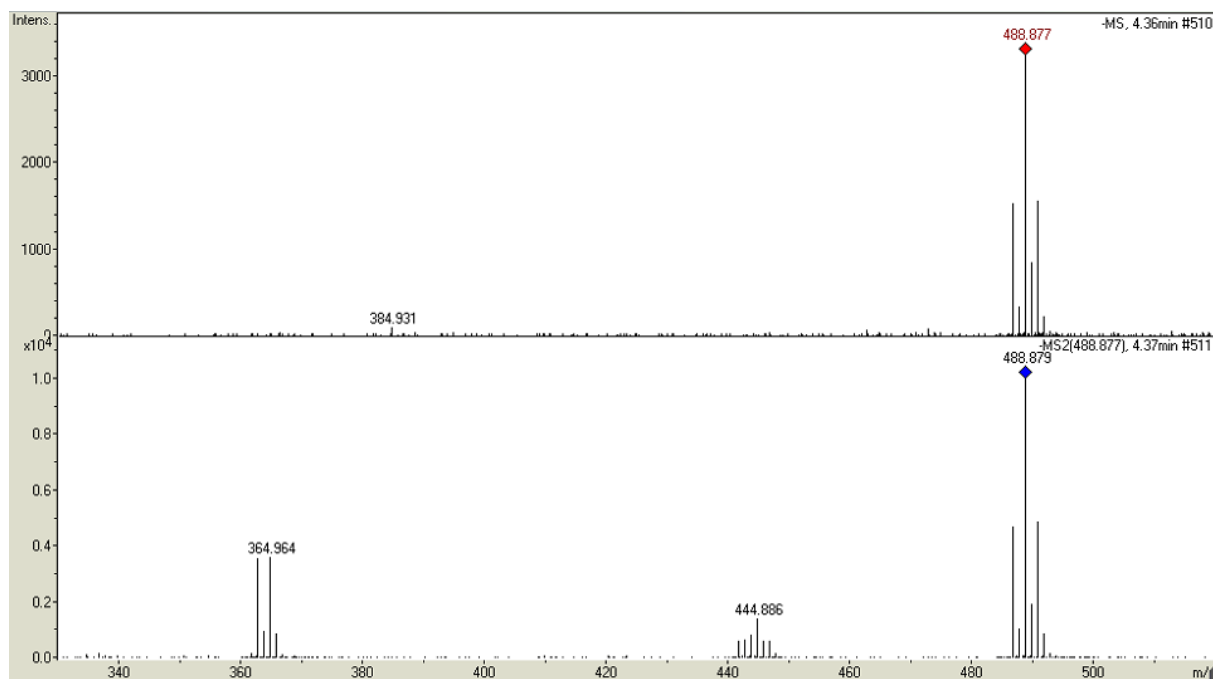


Figure S-12 - MS/MS spectra of eosin after the loss of two bromine atoms (m/z 488.88).

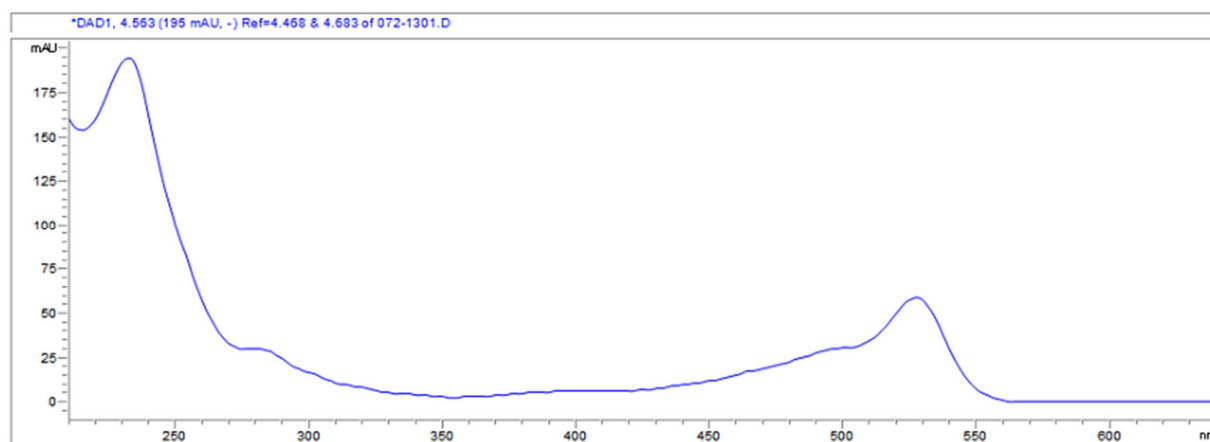


Figure S-13 – UV-vis spectrum of eosin after the loss of two bromine atoms (marked 3 in Figure 5). It should be noted that the spectrum is not pure due to (partial) co-elution.

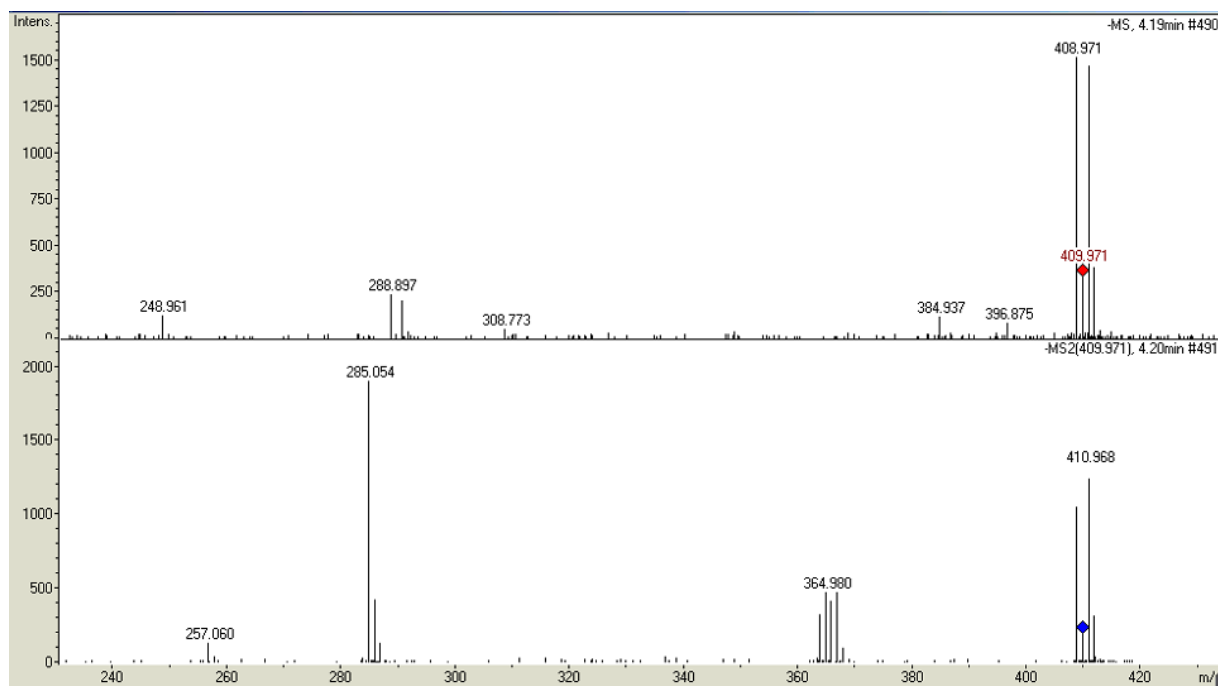


Figure S-14 - MS/MS spectra of eosin after the loss of three bromine atoms (m/z 410.97).

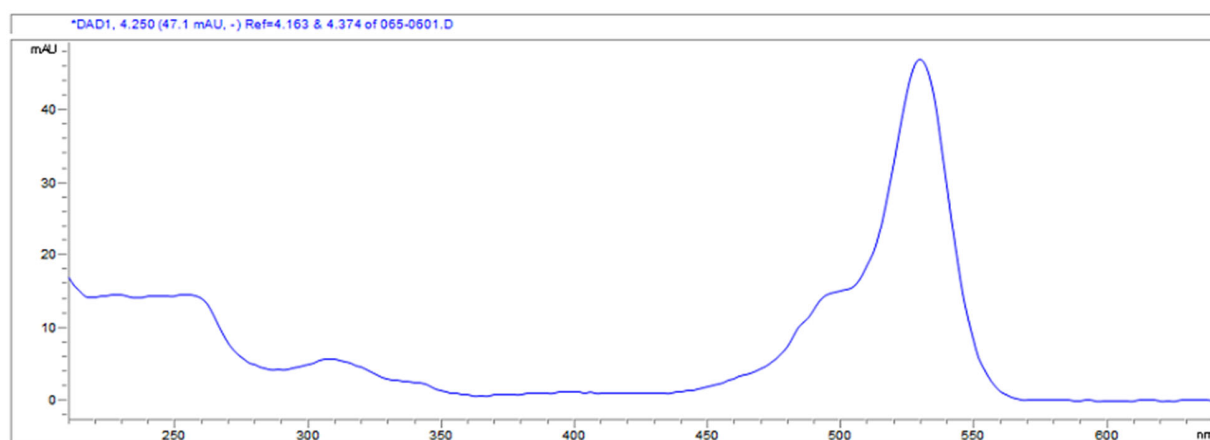


Figure S-15 – UV-vis spectrum of eosin after the loss of three bromine atoms (marked 4 in Figure 5). It should be noted that the spectrum is not pure due to (partial) co-elution.

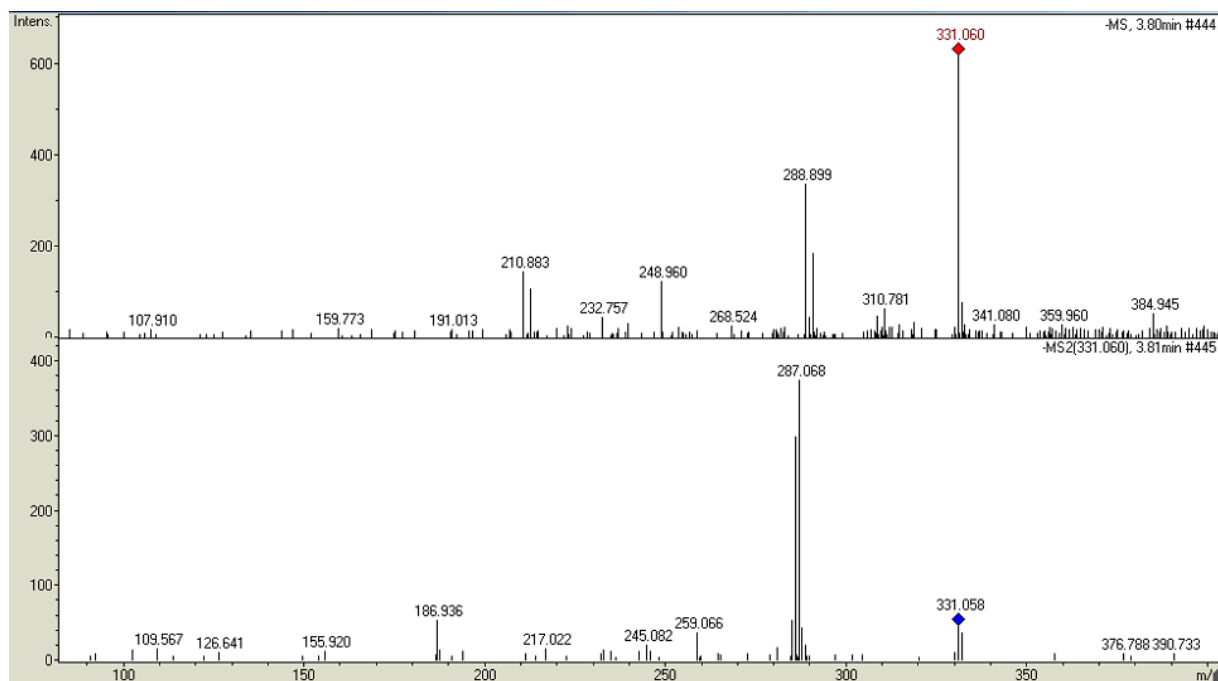


Figure S-16 – MS/MS spectra of uranin (eosin without all of its Bromine atoms) at m/z 331.06.

S-8 MS/MS data for methylated eosin

The MS/MS spectrum shown below was used to confirm the methylation of eosin.

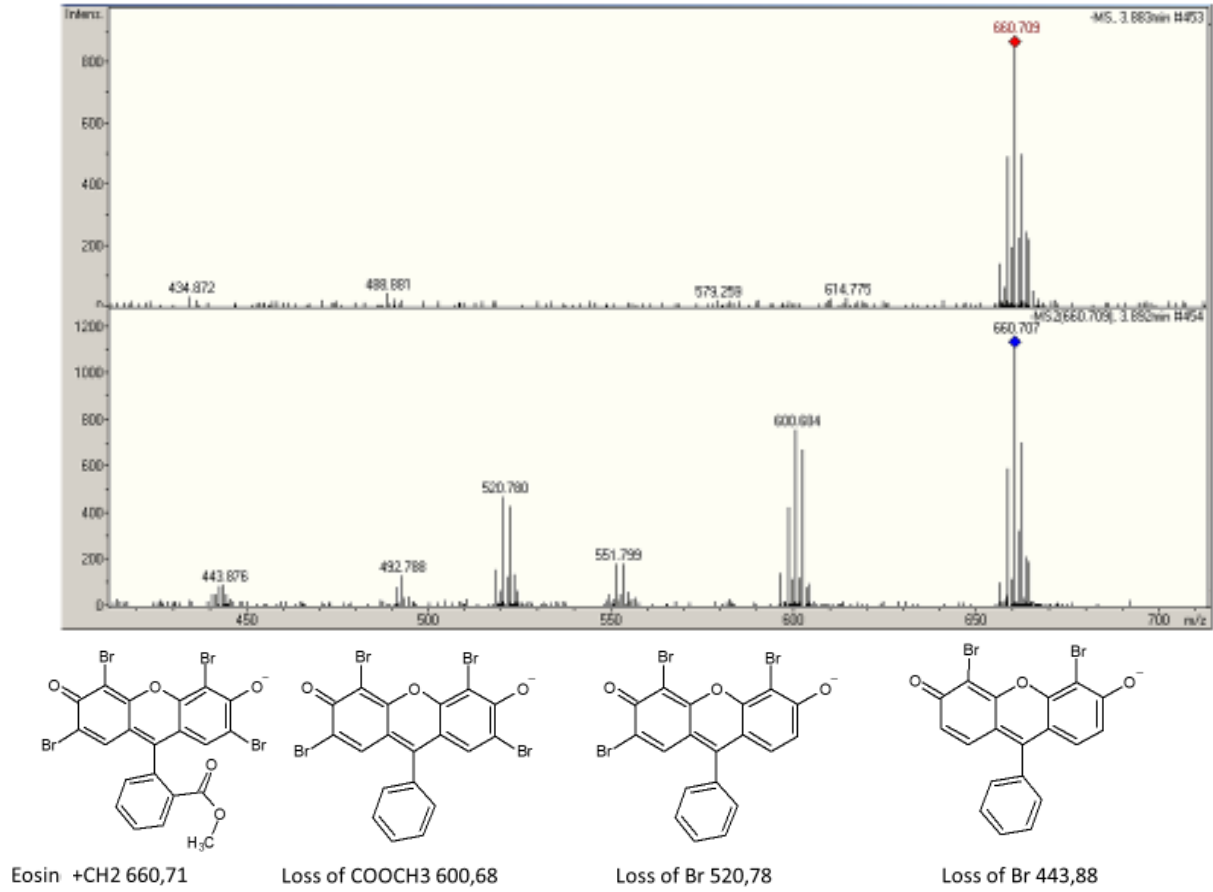


Figure S-17 - MS/MS spectra for methylated eosin with a clarification of the molecular structures.

S-9 MS/MS and UV-vis data for unknown main degradation product of eosin

Using the data shown in this section, a possible molecular structure was proposed in the main article. One key aspect is the apparent loss of the molecular-structure fragment shown below.

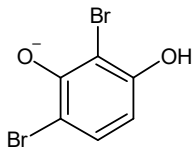
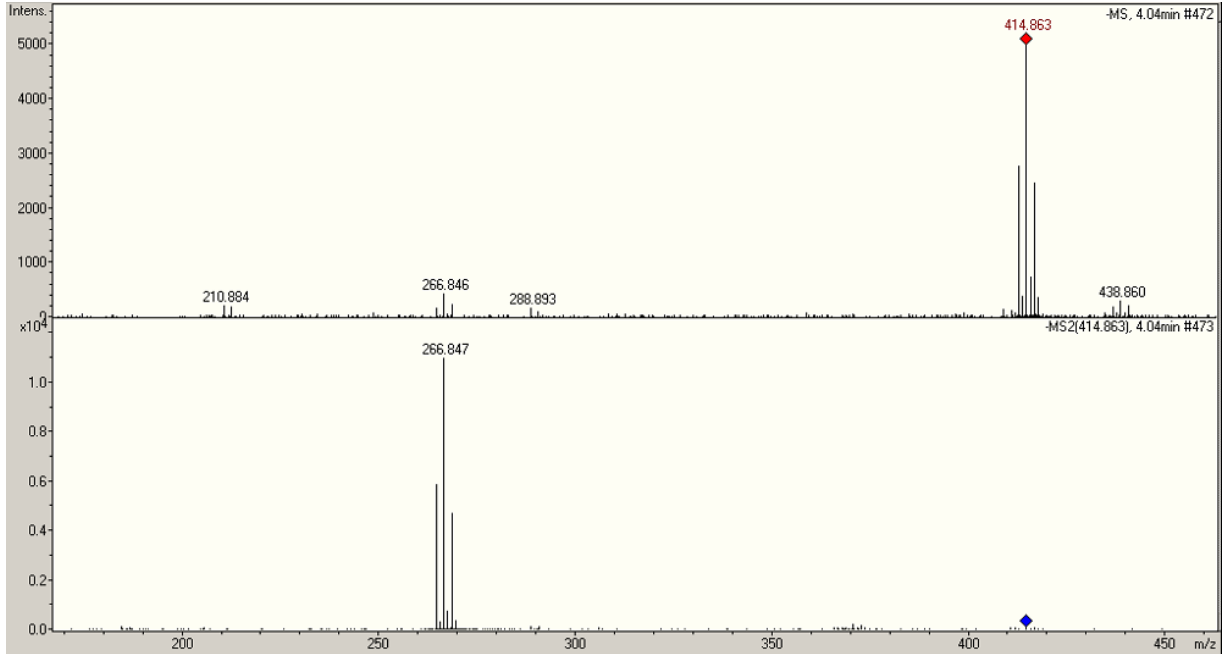


Figure S-18 – MS/MS spectra of main, unknown degradation product of eosin of m/z 414.86. The mass-to-charge ratio of 266.95 corresponds to the structural formula provided above. The isotope pattern confirms the presence of two remaining bromine atoms.

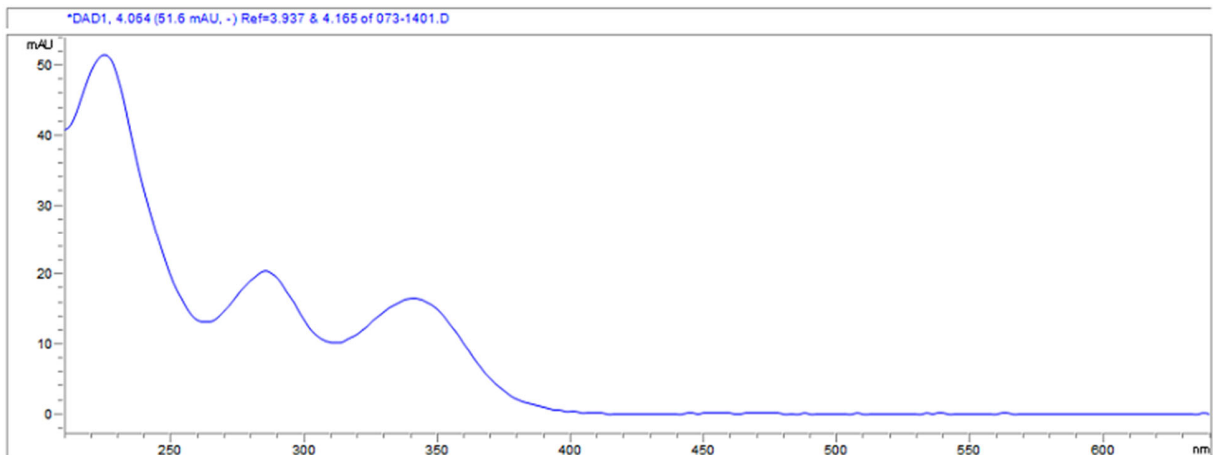


Figure S-19 – UV-vis spectrum of unknown degradation product of eosin of m/z 414.86.

S-10 MS/MS and UV-vis data for oxygenation of eosin

The following data were obtained for the oxygenated and methylated-oxygenated eosin molecules.

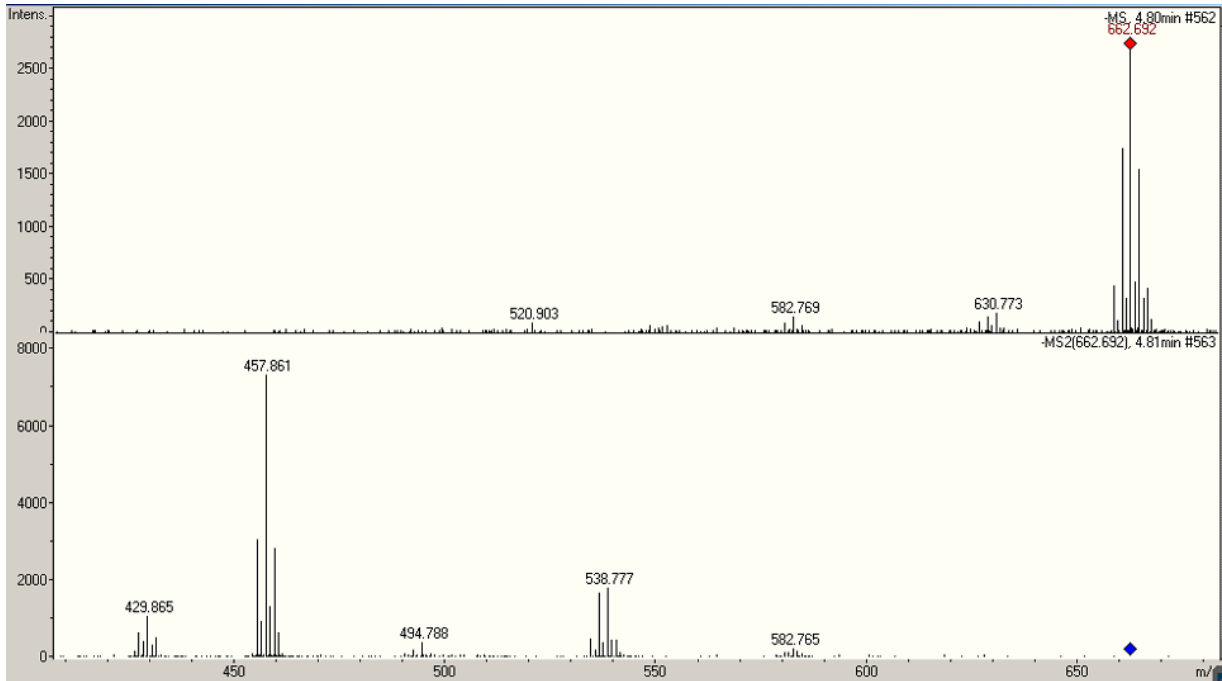


Figure S-20 – MS/MS spectra for oxygenated eosin (O1 in Figure 5).

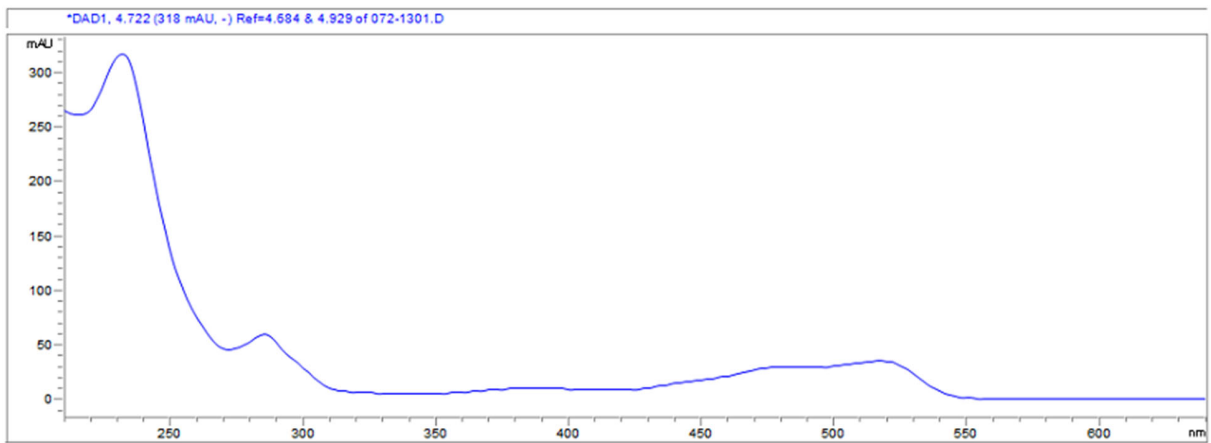


Figure S-21 - UV-vis spectrum of oxygenated eosin (marked O1 in Figure 5).

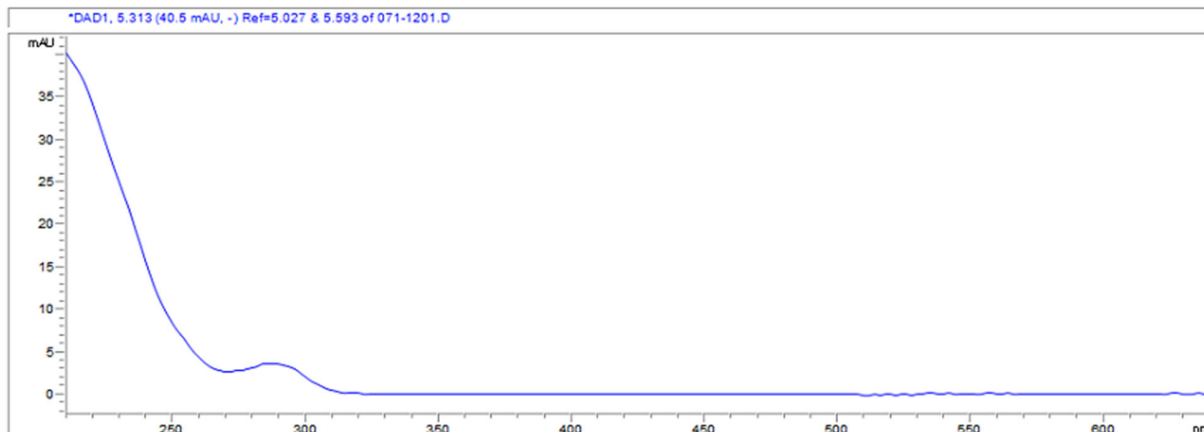


Figure 22 - UV-vis spectrum of oxygenated, methylated eosin (marked MO1 in Figure 5).

S-11 Oxygenation under influence of light by interaction with hydroperoxides

The proposed reaction mechanism below gives a possible explanation for the observed oxygenation of eosin under the influence of light [8]. The authors acknowledge Rien Reijneveld for compiling this overview.

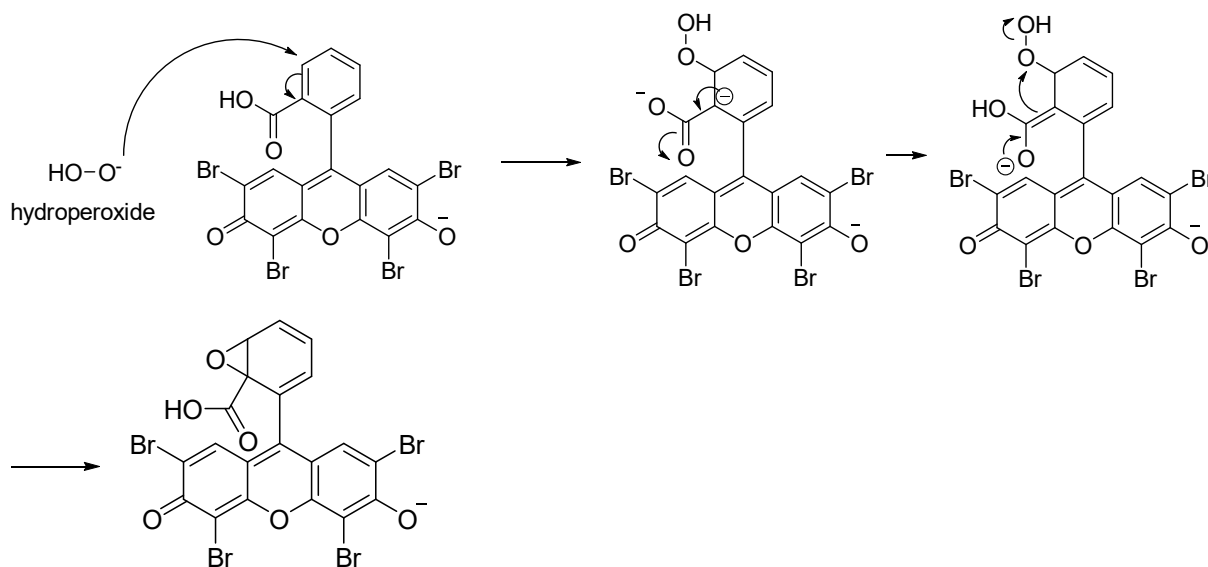


Figure S-23 – Example of possible clarification for the oxygenation of eosin.

S-12 Proposed structure for main degradation product of eosin

The following reaction is proposed for the formation of the main degradation product of eosin based on literature [9].

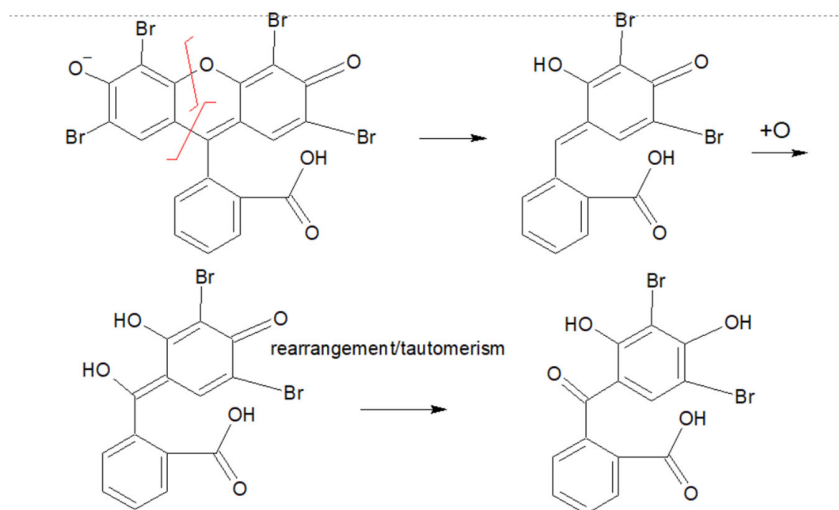


Figure S-24 - Proposed structure and mechanism for unknown main degradation product of eosin with mass 414.86.

S-13 Technical data Xenotest 150 S Heraeus

Instrument: Xenon 130 mm vertical arch 1300 W, air cooled. Spectral range: 300 - 830 nm. Energy emitted: 1154 W/m². Filters: UV cutoff 310 nm, IR (corresponding to "solar radiation through a glass"). Black cell temperature: 40°C. Relative humidity: not controlled. During the experiments for this work, the relative humidity of the Xenotest was between 50 and 60%. Sample exposure: The homogeneity of the exposure of different samples is ensured by rotation of sample holders around the light source (Fig. S-25, left). The exposure can be continuous or alternate (1 iteration exposed to the source, then 180° holder rotation and 1 iteration not exposed). Rotation speed: about 5 iterations/min. A total of 10 sample holders 130 × 45 mm are present. Thus, in alternate-exposure mode, a total of 20 sample holder slots are available. One half of each sample can be protected with black paper band (Fig. S-25, right).

The ageing was kindly performed by Witold Nowik (CNRS-C2RMF, France, within the framework of an H2020 funded project, IPERION-CH, GA 654028).



Figure S-25 – Left: rotating sample chamber. Right: Example of holders containing textile samples.

References

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