A letter to reply the comments

Title: Optical properties and oxidative potential of aqueous-phase products from OH and $^3C^*$-initiated photolysis of eugenol (acp-2021-895)

Dear Editor

We would like to very much thank you for the comments regarding our manuscript. These comments are very helpful for us to improve our paper. We have carefully revised the manuscript accordingly. A thorough grammar and spelling check of the manuscript were also done. Our point-to-point responses to your comments are listed below.

Response for major comments:

1) I still share Referee #3's concern that the manuscript reads like a lab report rather than a scientific paper. The various experiments are listed but the connection between the experiments and their conclusions are not fully clear. It would help if you referred to the various subsections within Section 3 to connect your results (e.g. can the kinetics be related to the reaction mechanism, how does the production of HULIS relate to the reaction mechanism etc?)

Response: Thanks. We enhanced some links among experimental results, mechanism and products in revised manuscript. For instance, in Section 3.2.4 "Thus, the decrease of pH value might be related to formation of organic acid and HULIS since carboxylic acids are possibly abundant in HULIS (Huo et al., 2021; Salma et al., 2008)."; Section 3.4 "Thus, we inferred that more higher molecular weight HULIS were formed at the first stage due to oligomerization and functionalization as suggested by Jiang et al.(2021), which consequently contributed to fluorescence at Ex of 400 nm (Barsotti et al., 2016).", Section 4 "Significant absorption enhancement over the range of near-UV region (300-400 nm) pointed out the continuous generation of BrC (i.e., HULIS). Direct HULIS concentration determination confirmed that HULIS was formed continuously over the course of reaction. Consequently, these light-absorbing products contribute to fluorescence at EX of 400-500 nm. GC-MS analysis confirmed the formation of high molecular weight multi-functional organic compounds, which has also been reported previously in similar aqueous phenolic photochemical experiments (Jiang et al., 2021; Misovich et al., 2021; Tang et al., 2020; Yu et al., 2014). Overall, our work shows that

SVOCs-aqSOA is an important source of BrC, therefore aqueous chemical processes may play a role in aerosol light absorption, radiative forcing, as well as climate change. In-depth molecular-level characterization or functional groups with respect to HULIS should be carried out in the future study”. Furthermore, we also reorganized Section 3.6.1 in order to establish connect between product and mechanism.

2) A lack of a coherent discussion was also expressed by Referee #1 who asked you to comment on the atmospheric relevance of the oxidant concentrations and their ratios. Therefore, I suggest that you add a separate section on the discussion of the atmospheric relevance of your results. Please also include a brief discussion on the representativeness of eugenol, and how its reactivity can inform about SOA processing (formation and loss) by precursors of intermediate volatility.

Response: We have supplement atmospheric relevance in Section 4 “Conclusions and atmospheric implication” in the revised manuscript. Furthermore, in Sect. 1 “Introduction”, we added some description about precursor eugenol. “In the present work, we choose 4-allyguaiacol/eugenol, as a model compound to conduct aqueous phase reaction. Eugenol, a representative methoxyphenol emitted from biomass burning (Hawthorne et al., 1989; Simpson et al., 2005), was widely detected in atmospheric particles. For instance, emission concentration and factor emitted from beech stove were 0.032 μg/m^3 and 1.534 μg/g, which are twice of those of (0.016 μg/m^3 and 0.762 μg/g) guaiacol (Bari et al., 2009; Liu et al., 2019). Eugenol is a representative semivolatile aromatic compounds with moderate water-solubility (2.46 g/L at 298 K).”

3) You discuss the formation of HULIS and it seems at some places that you exchangeable use HULIS with aqSOA. Please define what HULIS are in your discussion and how ‘humic-like’ and atmospherically-relevant these products formed in the reactions are (cf. e.g. discussion by (Graber and Rudich, 2006)). Please check carefully your discussion of HULIS and how comparable the products in your experiments are to HULIS as referred to in the literature (e.g. line 672).

Response: Thanks for your attention. We have paid attention this issue and revised it in this new manuscript. In section 3.4, we referred some discussion by Graber and Rudich. “The EEM spectra found new prominent fluorescent peak at Ex/Em=250 nm/400-500 nm, which was likely attributed to chromophores of HULIS. Humic substances are subdivided into fulvic acid (water soluble at all pHs), humic acid (base soluble, acid (pH 1) insoluble) and humin (insoluble at all pHs). In principle, extracted HULIS with polymer-based HLB SPE packing included LMW organic acids, fulvic acids or other humic substances. As suggested by Graber and Rudich (2006), two distinct ranges have been found to characterize humic substances: Ex/Em=330–350/420–480 nm (fulvic-like), and Ex/Em=250–260/380–480nm (humic-like). So, we inferred most HULIS in this paper was humic-like substance rather than fulvic-like substance."

Response for minor comments:

1) l. 37/38: Keywords are not needed

Response: Deleted.

2) l. 58: I share the referee #2's concerns that you do not properly cite previous literature on aqueous phase oxidation of organics, in particular of phenolic compounds. A huge number of kinetic and product studies for small VOCs and also for phenolic compounds have been performed before 2010 (the oldest currently cited paper here). Please cite also relevant older references of the aqueous phase oxidation of phenolic compounds. See for example review articles (Herrmann, 2003; Herrmann et al., 2015) and specific other studies (Barzaghi and Herrmann, 2002; Bonin et al., 2007; Sun et al., 2010)

Response: We have cited many relevant older references of the aqueous phase oxidation of phenolic compounds.

3) l. 80/81: There are numerous studies that clearly state the role of ROS (including OH, H2O2) for SOA formation. Please include appropriate literature or revise this sentence.

Response: This sentence has been changed to "Despite strong evidence in support of the importance of ROS in photochemical process (Ma et al, 2021;Wang et al., 2020; Wang et al., 2021; Wu et al., 2021), however, our understanding on SOA from $^{3}C^{*}$-initiated reaction is still limited."

4) l. 260: A 'rate' refers to a speed of a process; therefore, it has units of 1/time or concentration/time. Please clarify what □ is. I assume you mean 'degree of degradation' (dimensionless)(?)

Response: Thanks for your attention. "degradation rate" has been replaced by "degradation efficiency".

5) l. 319-338: This text needs to be clarified and further elaborated on (see also Referee#1's comment 1). It needs to be made clear whether these findings of the relative importance are only valid under your experimental conditions or also to the atmosphere.

Response: Thanks for your suggestion. Other studies (Laurentiis et al., 2013; Misovich et al., 2021) of aqueous DMB-photosensitized reaction also showed $^3C^*$ was the greatest contributor to phenol or guaiacyl acetone loss, followed by $^1O_2$, while both •OH and $^1O_2$ contributions were relatively minor(Section 3.2.1).

6) Section 3.5.1: How do the aqSOA yields compare to those reported in other studies, e.g. (Ma et al., 2021; Smith et al., 2014)? Why do you find different values than in your previous study?

Response: We have reorganized Section 3.5.1: The SOA mass yield are slightly higher than value (ranging from 80-140%) from phenol-triplet reaction (Ma et al., 2021; Smith et al., 2016; Yu et al., 2014). For the same oxidation time, mass yields from $^3C^*$oxidation were generally higher than those from OH-initiated oxidation and direct photolysis. These results were similar to investigation on aqueous oxidation of phenolic compounds (Smith et al., 2014, 2015, 2016). There are two plausible reason for high masses for $^3C^*$-initiated oxidation. Firstly, oxidation by $^3C^*$ was more efficiently to form oligomers and functionalized/oxygenated products (Richards-Henderson et al., 2014). Higher oxidative degree of aqSOA from $^3C^*$-initiated photooxidation (see Sec.3.5.2) warrants above hypothesis. Secondly, more light-absorbing products (i.e. HULIS) can participate in SOA formation by acting as photosensitizers (Tsui et al., 2018).

7) Section 3.6.2: How quantitative is this reaction mechanism? Were all intermediates and products identified by GC-MS or were some inferred?

Response: All the products (colored and numbered) were identified by using GC-MS. Some of them (Eugenol, DMB, product 1, 2,5) were identified by using certified reference materials, some of them (product 3, 4, 9)identified by matching the NIST database, and others (product 6, 7, 8) were inferred according to the molecular ion peak and fragments from GC-MS, combine with NIST matching results and the start material & reaction conditions. The other intermediates and the mechanism were inferred and proposed according the identified products and the reaction rationality from start material. Corresponding description has been added in Section 3.6.1 and 3.6.2. All the

MS spectrums for Eugenol, DMB and products 1~9 were listed as following.

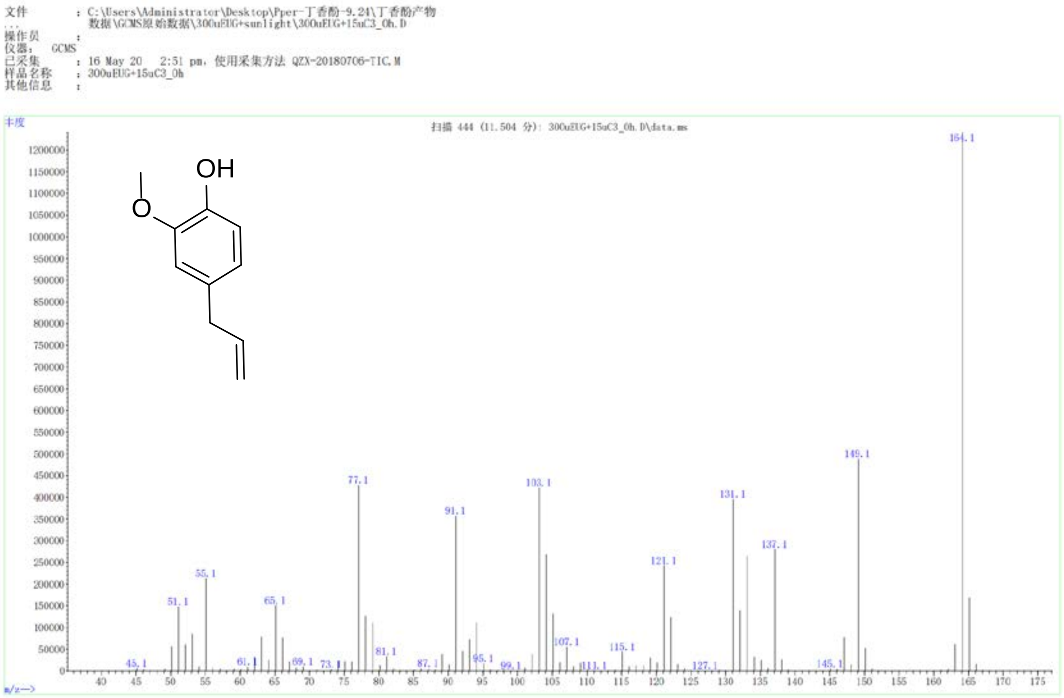

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Fig 1. Eugenol, t = 11.50 min

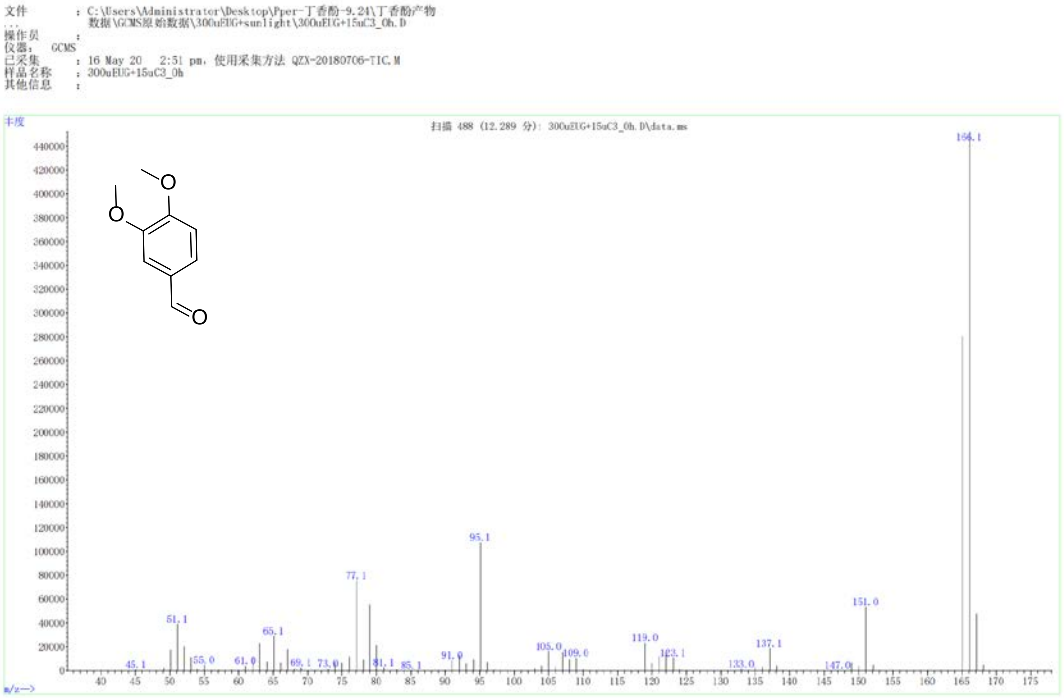

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Fig 2.DMB , t = 12.29 min

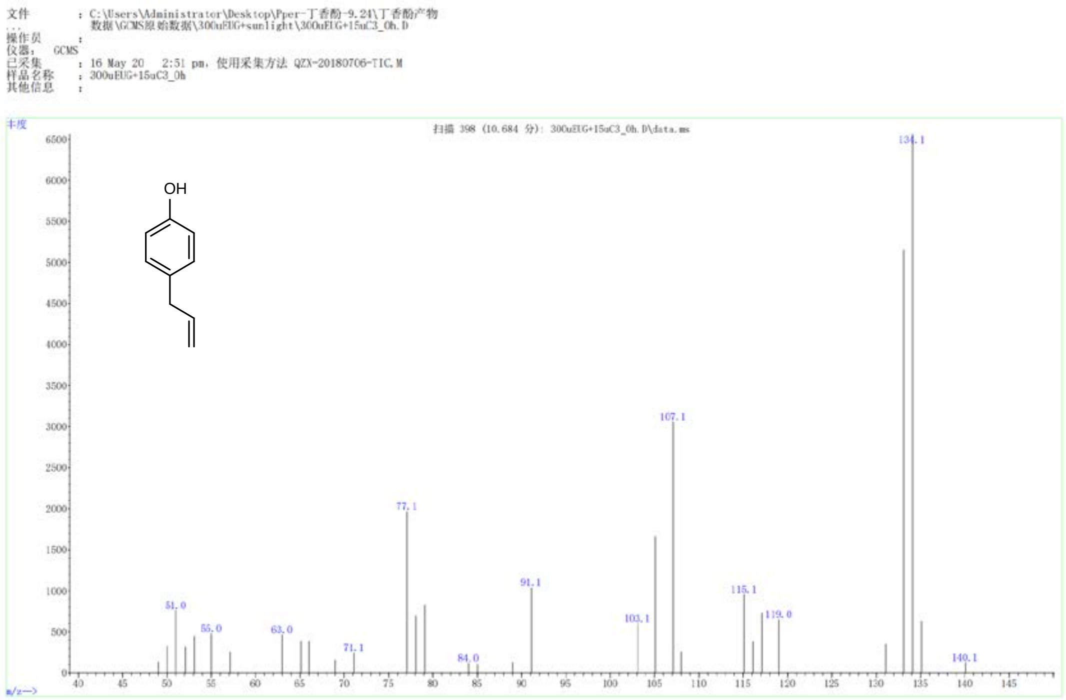

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Fig 3. Product 1, t = 10.68 min

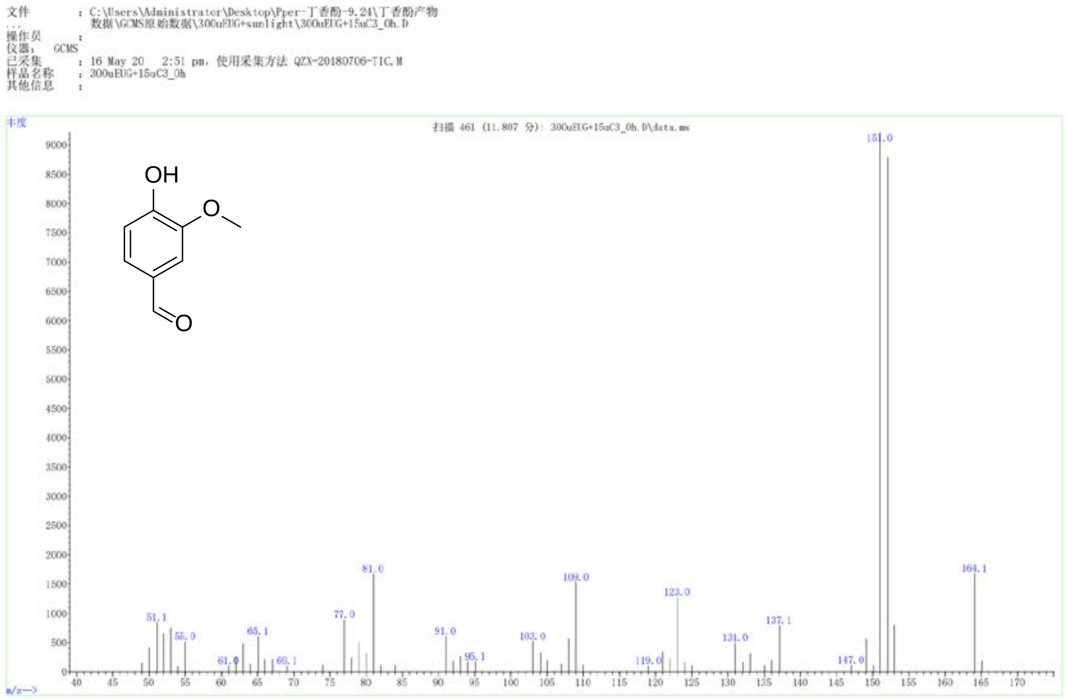

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Fig 4. Product 2, t = 11.81 min

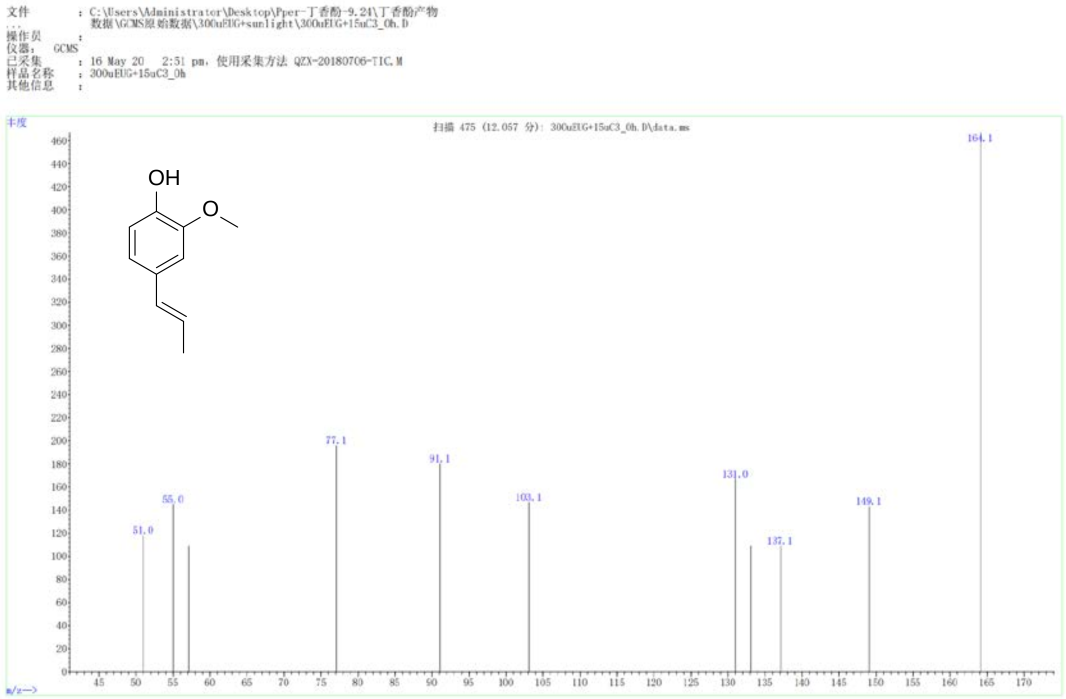

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Fig 5. Product 3, t = 12.06 min

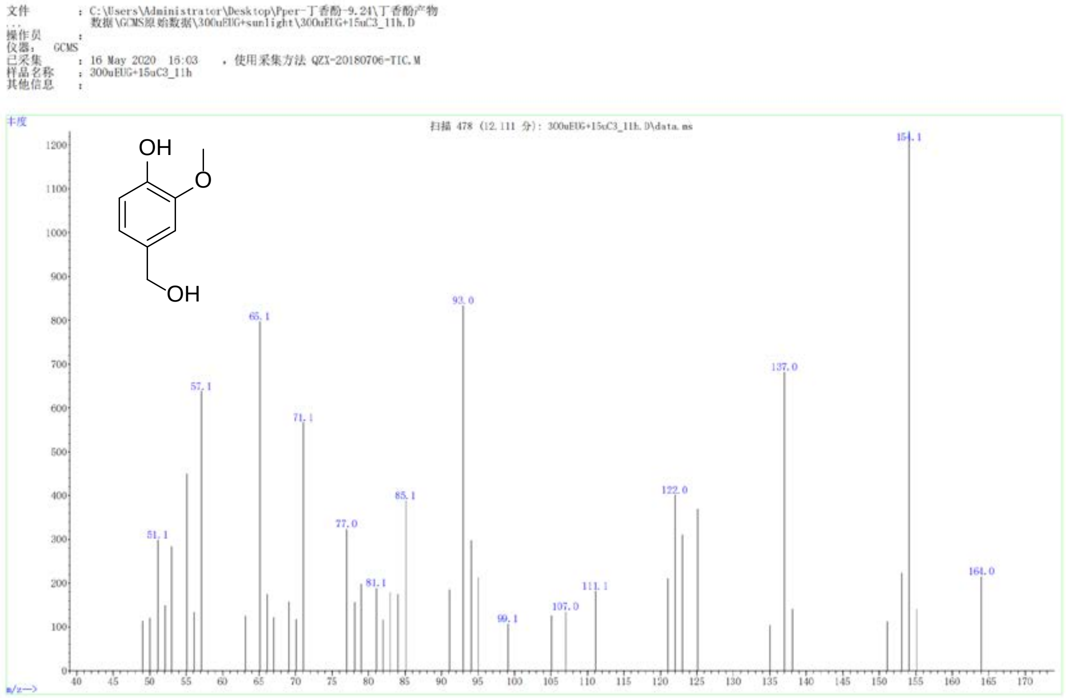

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Fig 6. Product 4, t = 12.11 min

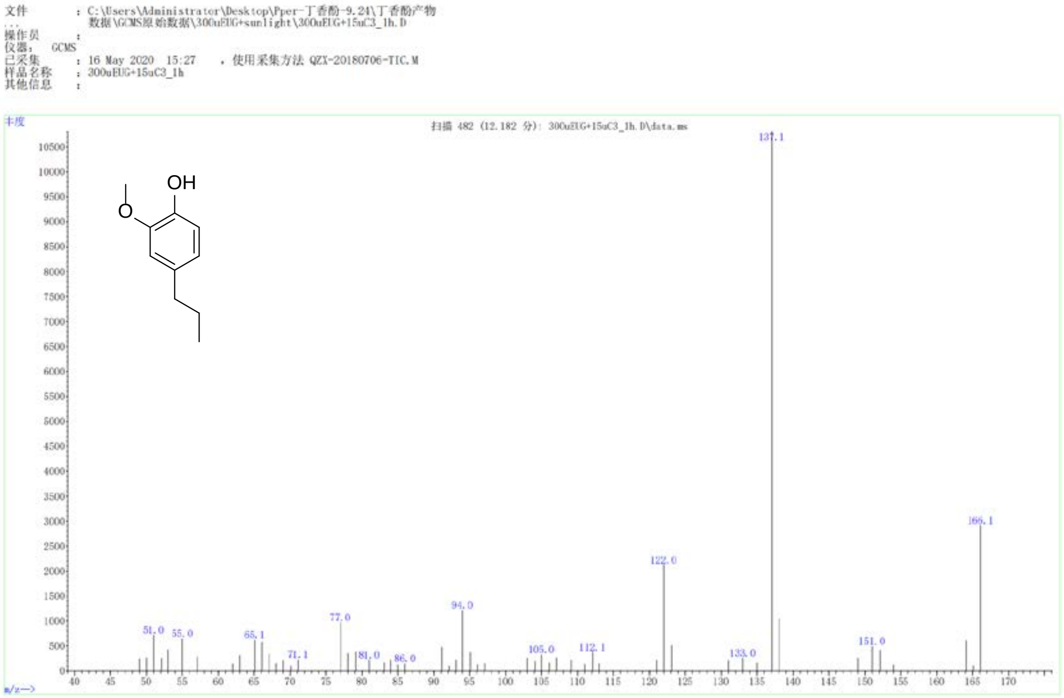

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Fig 7. Product 5, t = 12.18 min

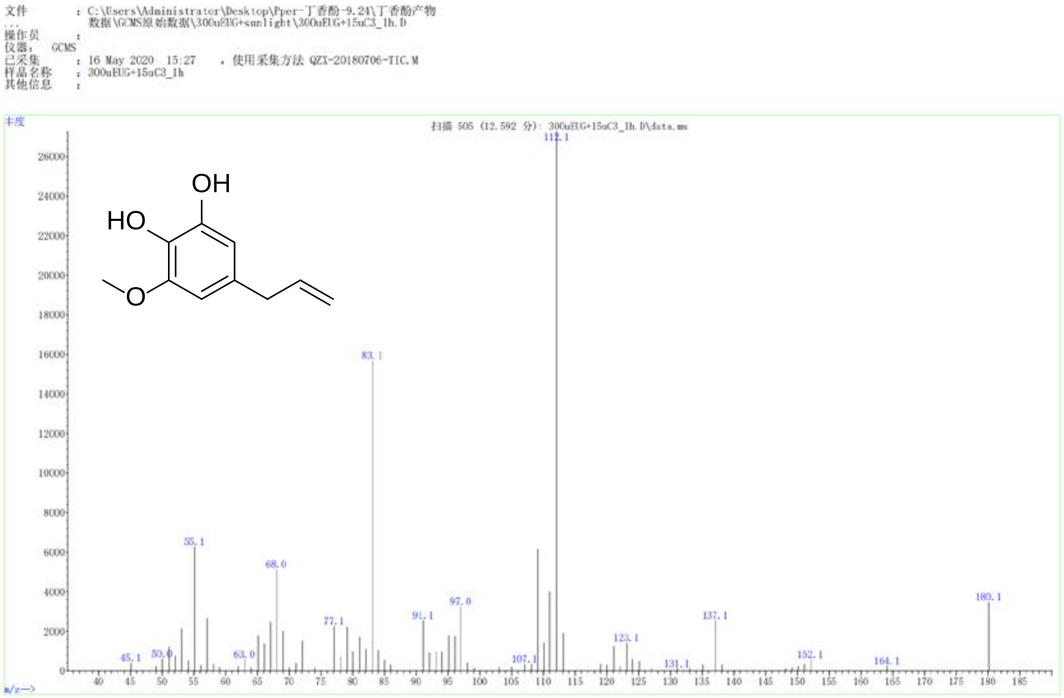

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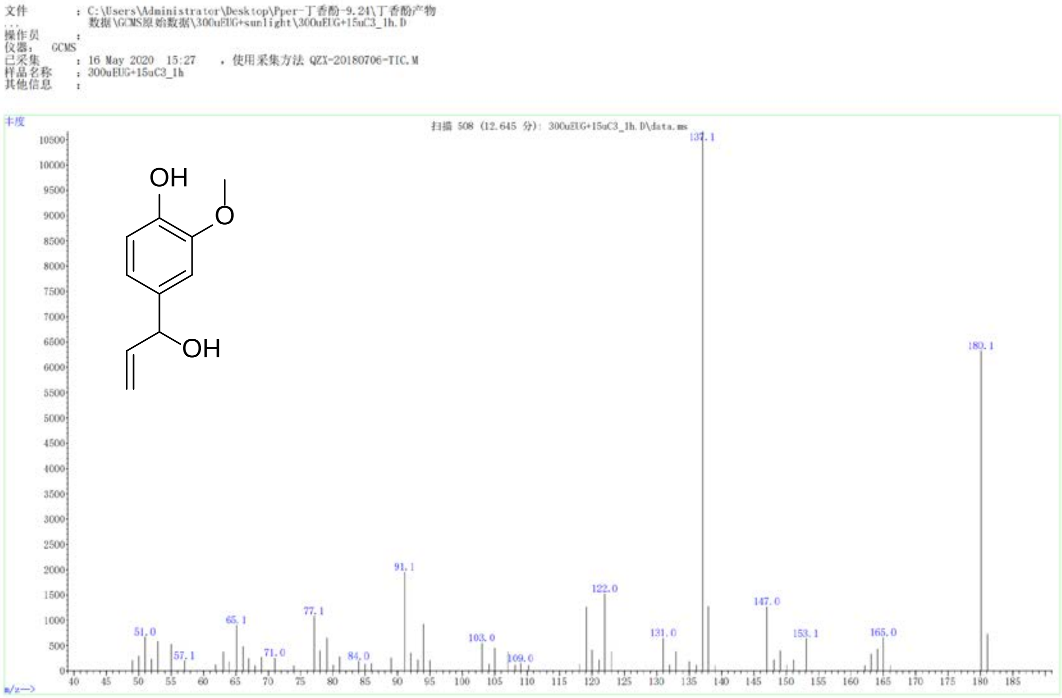
Fig 8. Product 6, t = 12.59 min



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其他信息：

Fig 9. Product 7, t = 12.65 min

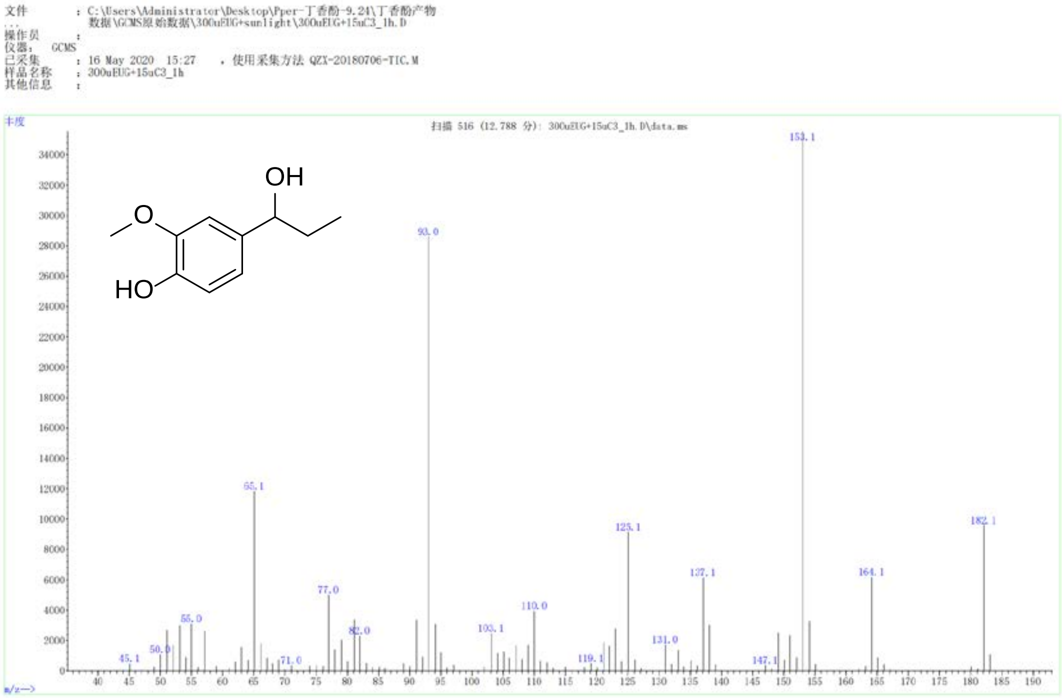

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Fig 10. Product 8, t = 12.79 min

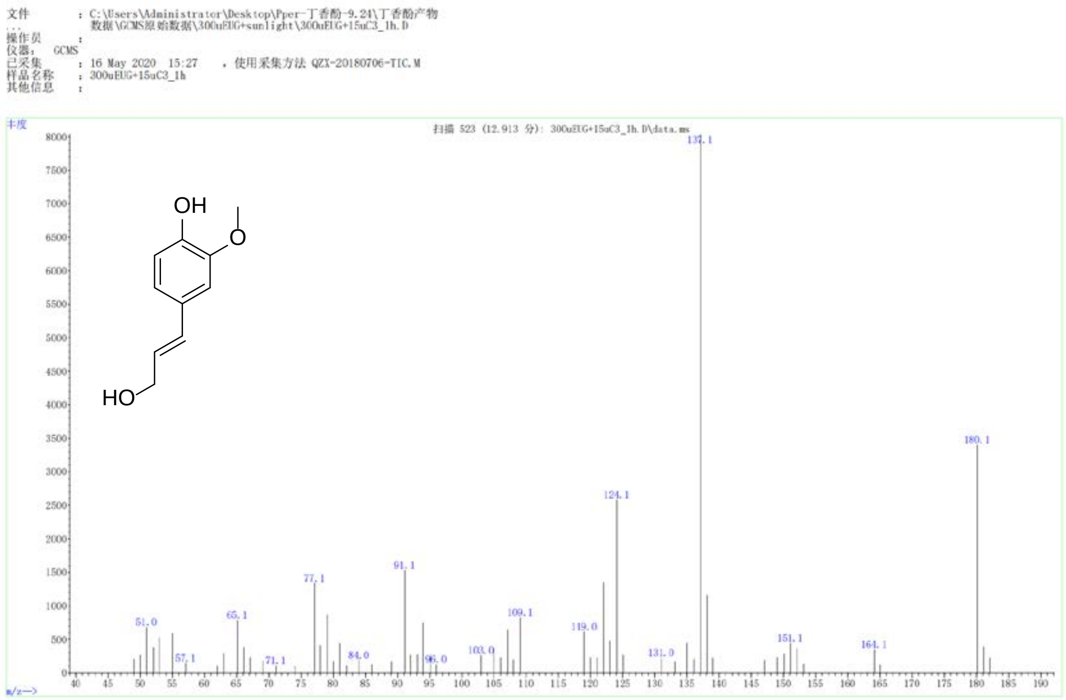

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Fig 11. Product 9, t = 12.91 min

III. Technical comments

Please carefully proofread your manuscript and correct unclear language, grammar mistakes and typos. I added a long, but not exhaustive list below.

Response: Thanks for your suggestions. We have rewritten some paragraphs and made major revisions especially add more discussion for this manuscripts to make it easy to follow. We have also corrected typographical errors, grammatical inaccuracies, misspelling, and so on, we hope the new version meets the journal’s requirement.

l. 18: ‘under two radicals’ should be ‘in the presence of radicals’

l. 22: define ‘ESP’

l. 45: replace ‘are’ by ‘is’ (aqSOA is singular)

l. 46: either ‘less volatile’ or ‘have lower volatility’

l. 51: ‘not yet’ is redundant

Response: Done.

l. 61/62: This sentence is not clear.

Response: This sentence has been optimized to “Generally, chemical structure of precursors has significant influence on aqSOA and reaction mechanisms, however, the effect of oxidant on SOA formation also cannot be neglected.”.

l. 63: I assume you do not mean 1O2 (singlet oxygen) and not molecular oxygen.

Response: Yes. We mean singlet oxygen and replaced it.

l. 66: ‘predominant oxidant’ is ambiguous. It is correct that the rate constants of OH reactions are usually much higher than those of the NO3 radical or other oxidants. However, other oxidants (such as H2O2 or 1O2 (singlet oxygen) might be equally high or even higher)

Response: We totally agree with you. ‘predominant’has been changed to “ubiquitous” to make sense.

l. 93/94: Why can vanillic acid be considered a proxy for HULIS?

Response: This sentence has been changed to ‘Subsequently, numerous studies have observed light-absorbing products formed in aqueous photodegradation and further verified that aqueous reaction was a potential source of HULIS (Li et al., 2021; Smith et al., 2016; Tang et al., 2020)’.

l. 100/101: (1) Please add a reference to this sentence. (2) replace ‘served’ by ‘serve’.

Response: Done.

l. 107: replace ‘has’ by ‘have’

Response: Done.

l. 120/121: What do you mean by ‘deeply clarifying the degradation mechanism’?

Response: This sentence has been optimized to ‘The relative importance of various ROS species to eugenol degradation was explored in order to clarify reaction mechanism.’

l. 142/3: ‘At the bottom of sample tubes, there are fan and magnetic stir bar to make solution full mixed’ – reword, e.g. ‘To ensure mixing of the solution, a fan and a magnetic bar are placed at the bottom of the solution’.

Response： Thanks. We have revised according to your suggestion.

l. 150/1: ‘slightly lower’ is not correct, if you refer to light intensity that is more than 60% lower than sun light.

Response: ‘slightly lower’ has been replaced by ‘was lower’.

l. 159: replace ‘darkness’ by ‘dark’

l. 161: replace ‘now’ by ‘not’

l.201: replace ‘was’ by ‘were’

Response: Done.

l. 222: ‘for distinguish’ – do you mean ‘as a blank’? Please clarify.

Response： Yes. We mean distinguish between blank and solution reaction. So, we rewritten this sentence: Another 1.2 mL ultrapure water instead of sample solution was treated in the same way and absorbance was denoted as A for distinguish from A_t.

l. 232: replace ‘Products’ by ‘Product’

l. 245: ‘CHO1’ should be ‘CHO’

Response: Done.

l. 280: Unclear what ‘they’ refers to. Are you referring to chemical bonds in general or to a specific bond referred to in the previous sentence?

Response: Thanks. We added ‘As we known’ before this sentence.

l. 285: Please reword this sentence, e.g., ‘The pseudo-first-order rate constants were obtained by fitting eugenol concentration to the equation [please add equation number here!]. The experiments were performed under conditions of excess oxidants.’

Response: Thanks. We moved this sentence to the upper of the first paragraph in Section 3.1. And this sentence has been optimized to ‘Figure 1 shows unreacted eugenol concentrations (c_t) and the negative logarithm of c_t/c_0 ($-\ln(c_t/c_0)$) as a function of reaction time, respectively. The pseudo first-order rate constant (k) obtained by Eq.(1) was also presented.’.

l. 290/1: I do not understand this sentence: Are you saying that the oxidation by 3C* is faster because it is a combination of multiple pathways including reactions with 1O2, O2- and OH? Please clarify.

Response: Yes. This sentence has been optimized to ‘$^3C^*$-initiated photodegradation was quicker than that with •OH due to contributions of combination of multiple pathways including reactions with $^1O_2$, $O_2^{-}\cdot$ and ·OH.’

l. 301: What does ‘they’ (were calculated) refer to? If you mean ‘the relative importance’, it should be ‘it’.

Response: Yes. ‘they were’ has been replaced by ‘it was’.

l. 349: replace ‘combing’ by ‘combining’

Response: Done.

l. 371 – 373: This sentence is not clear. Please clarify.

Response: Yes. This sentence has been optimized to ‘The *p*-BQ could quench $O_2^{\bullet-}$, which further suppress the generation of other ROS (e.g., $\bullet HO_2$), as a result, the rate constant decreased the most (from 2.73×10^{-4} s^{-1} to 1.20×10^{-4} s^{-1}), suggesting $O_2^{\bullet-}$ might be responsible for eugenol photodegradation’.

l. 371: Do you really mean ‘photolysis’ here or ‘photooxidation’?

Response： Yes. ‘photolysis’was replaced by‘photooxidation.

l. 374: add ‘by’ (decreased by 56%).

Figure 3: The labels next to the lines in all panels are really hard to read. Please improve the figure quality.

Response： Done.

l. 420: replace ‘directly’ with ‘direct’

Response: Done.

l. 424 – 426: This sentence is not clear. Please clarify.

Response: The first paragraph in Section 3.2.4 has been optimized to ‘As shown in Fig.4a, solution pH values decreased quickly at the beginning of illumination (from 7.4 to ~5.0 for the first 1h) then tended to smooth in both direct photolysis and OH-initiated oxidation. However, little change of pH value (less than 0.1 unit) was observed for the $^3C^*$-initiated photooxidation, which could be ascribed to very low initial pH value (pH=3). Generally speaking, slight increase of acidity cannot remarkably change pH value when original solution pH was very low. We cannot rule out formation of acid products at $^3C^*$-initiated oxidation. Thus, the decrease of pH value might be related to formation of organic acid and HULIS since carboxylic acids are possibly abundant in HULIS (Huo et al., 2021; Salma et al., 2008).’.

l. 439: replace ‘In a word’ by ‘In summary’

l. 497: fluorescent

l. 498: replace ‘more intense’ by ‘higher intensity’

l. 504: replace ‘photosensitise’ by ‘photosensitizer experiments’

Response: Done.

l. 510 – 517: What is the main message of this text? Please reword and clarify.

Response: Thanks. We have reword this section.

l. 519: ‘characterize aqSOA’ is too general. Do you mean molecular composition or structure, optical properties?

Response: Yes. We changed ‘characterize aqSOA’ to ‘characterize molecular composition’.

l. 500; l. 527: HULIS

Response: Done.

l. 592 – 594: Please correct and clarify this sentence.

Response: This sentence has been optimized to ‘The O/C was lower than that (0.85-1.23) of other phenolic aqSOA reported due to different substituted group in aromatic ring (Yu et al., 2014).’

l. 644: This sentence seems redundant.

Response: Thanks. We deleted this sentence.