Ozonation of triterpenoids: Implications for early diagenesis of biomarkers in oxic environments

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A B S T R A C T

This study examines the fate of commonly found organic natural products under exposure to ozone to simulate early oxic diagenesis. The model compounds β-amyrin, lupenone and friedelin have been investigated by ozonation in the presence of water. The transformation products were identified or proposed based on their fragmentation patterns in mass spectra. The double bonds located at the isopropenyl group of lupenone and ring C of β-amyrin are the main reaction sites in the ozonation reaction. The major products identified from the ozonation of β-amyrin are β-amyrone, 12,13-epoxyoleanan-3β-ol, 11-oxoolean-12-en-3β-ol, 12-oxooleanan-3β-ol. In addition, 8,14-seco-12-oxooleanan-14-en-3β-ol, 8,14-seco-12-oxoolean-13-en-3β-ol and 8,14-seco-oleanan-3,12-dione, generated from the bond cleavage between C-8 to C-14 of 12-oxooleanan-3β-ol and 12-oxooleanan-3-one, respectively, have also been detected. 22,29,30-trisnorlupan-18(19)-en-3-one, 22,29,30-trisnorlupan-3,19-dione, 22,29,30-trisnorlupan-3,12-dione, lupeol, lup-22(29)-en-3-on-29-ol, 22,29-epoxylupan-3-one, lupan-3-on-29-al, lupan-3-on-29-ol and 18,22-epoxylupan-3-one are the major products from the ozonation of lupenone. No transformation product was detected for friedelin, probably due to its stability to ozonation.

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1. Introduction

The reaction mechanisms affecting natural product biomarkers during early diagenesis are an important aspect of organic geochemistry. The major processes acting on organic matter and the associated compounds in the ambient oxic environment are biodegradation (e.g. Deming and Baross, 1993; Hinrichs, 1993), oxidative attack (e.g. ozone, hydroxyl radical, others; Atkinson and Carter, 1984; Atkinson et al., 1995), and photochemical alteration (e.g. Wheeler, 1972; Simoneit et al., 2009). It is oxidation that is of interest here. Volatile organic compounds react in the atmosphere with ozone, hydroxyl radical and NO3 radical, producing secondary aerosol particulate matter (Seinfeld and Pandis, 1998). Extensive experiments have been reported for gas phase ozonation reactions (e.g. Criegee, 1975). However, ozone tends to decompose in water to form hydroxyl radical which is the surrogate oxidizing agent (Hasson et al., 2003). The fate of natural product biomarkers adsorbed to or part of organic particulate matter in the ambient environment and exposed to such oxidants has not been investigated.

Ozonation has also emerged as an important technology for the destruction of a wide range of organic contaminants. The application of ozonation in drinking water treatment is widespread in Europe with lesser extent in the USA (Huber et al., 2004). The feasibility of ozonation in the treatment of sediments and soils has been extensively studied (e.g. Hong et al., 2008; Javorská et al., 2009; Russo et al., 2010, 2012; Filho et al., 2011; Mahanty et al., 2011). So far, the treatment of contaminated soils and sediments has largely focused on pollutants such as PAHs and PCBs. However, the ozonation of organic geochemicals always associated with sediments and soils, such as triterpenoids, has not been reported. Ozonation has been applied as an effective method to decompose specific organic contaminants (e.g. Ikehata et al., 2006; Benner and Ternes, 2009; Tay et al., 2009, 2010). Lastly, the introduction of oxygenated functional groups to triterpenoids can significantly affect their bioactivities (Mikhailova et al., 2007). Thus, it is necessary to know all the possible transformation products of triterpenoids that may possibly form in the environment by ozone exposure.

The main objective of this study is to identify the major transformation products generated from the ozonation of β-amyrin (I, all structures cited are given in Appendix A), lupenone (IX), and friedelin (XX) in water and also to propose the mechanisms for the transformation of these selected triterpenoids in the ozonation reaction. Due to the presence of a double bond in lupenone and β-amyrin, a variety of oxygenated derivatives are expected to be formed. These triterpenoids were selected as representatives of the oleanane, ursane, lupane, and friedelane skeleton classes common in terrigenous higher plants (Simoneit, 2008).

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2. Material and methods

2.1. Chemicals

β-Amyrin was obtained from Fluka, USA, friedelin from Spectrum Chemicals, USA and lupenone from Carl Roth KG, Germany and all used without further purification. All solvents were purchased from Merck (Germany), of high performance liquid chromatography (HPLC) grade and used without purification. Phosphate buffer at pH 7 (0.5 M) was prepared using sodium dihydrogen-phosphate (Aldrich, USA) and/or disodium hydrogen-phosphate (Riedel-de Haen, Germany). Silica gel (Pharmprep) was purchased from Merck (Germany). β-Amyrin, friedelin and lupenone with the concentration of 200 mg/l were prepared by dissolving these compounds in dichloromethane. A mixture of BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide) and TMSCl (trimethylchlorosilane) in a ratio of 99:1 was obtained from Supelco (USA).

2.2. Ozonation

Due to the low solubility of the selected compounds in water, they were first coated on silica gel. Two ml each of the β-amyrin, friedelin and lupenone stock solutions were mixed separately with 1 g of silica gel. The solvent was then evaporated to dryness using a rotary evaporator. Selected compound coated silica gel was dispersed in 50 mM phosphate buffer (pH 7) solution in a conical flask. Ozone was produced from purified oxygen (99.8%) by an OZX-05K model ozone generator (Enaly ME Ltd., Shanghai, China). O₃ at the concentration of 0.70 g/h was continuously bubbled into the stirred solution through a gas dispersion tube placed at the bottom of the conical flask for 5, 10, 15 and 30 min. The reaction was quenched at the defined time intervals using nitrogen gas to remove the residual ozone and the mixtures were liquid–liquid extracted using dichloromethane. Then, the extracts were silylated using BSTFA and TMSCl (99:1) mixture for 4 h at 70 °C. Silylated extracts were dried using a nitrogen stream and re-dissolved in 250 μl of dichloromethane. A 1.0 μl aliquot of the solution was injected into the gas chromatograph-mass spectrometer (GC–MS) for analysis.

2.3. GC–MS analysis

The extracts were analyzed on a Shimadzu GC–MS system (GCMS-QP2010-Plus, Kyoto, Japan) equipped with an Rtx-5MS column (Crossbond 5% diphenyl/95% dimethyl polysiloxane, 30 m × 0.25 mm I.D., 0.25 μm, Restek, Bellefonte, PA). Helium (purity 99.999%) with an average velocity of 40.2 cm/s was used as the carrier gas. The GC oven temperature program was as follows: isothermal at 60 °C for 2 min, 60–150 °C at 30 °C/min, then 150–310 °C at 4 °C/min and hold at 310 °C for 10 min. The injection port and transfer line were maintained at 300 and 310 °C, respectively. The data for quantitative analysis were acquired in the electron impact mode (70 eV) over the mass range of 50–700 Da.

3. Results and discussion

In this study, the reaction between ozone and triterpenoids adsorbed on silica gel as model carrier was investigated. Silica gel is often used to investigate the environmental heterogeneous reactions of different pollutants such as polycyclic aromatic hydrocarbons (Alebic-Juretic et al., 1990, 2000), methacrolein and methyl vinyl ketone (Chen et al., 2008). Silica gel had been chosen because it has been used to adsorb ozone for storage and atmospheric ozone analysis purposes (Rubin, 2008). The adsorbed ozone on the surface of silica gel is reported to be stable and therefore, silica gel can be a good solid support to study the reaction between ozone and triterpenoids.

![Fig. 1. GC–MS TIC traces of selected triterpenoids after ozonation. β-amyrin-TMS (I), β-amyrone (II), 12,13-epoxyoleanan-3β-ol-TMS (III), 8,14-seco-12-oxo-oleanen-3β-ol-TMS (IV), 8,14-seco-12-oxo-oleanan-3β-ol-TMS (V), 11-oxoolean-12-en-3β-ol-TMS (VI), 12-oxo-oleanan-3β-ol (VII), 8,14-seco-olean-3,12-dione (VIII), lupenone (IX), 22,29,30-trisnorlup-18(19)-en-3-one (X), 22,29,30-trisnorlupan-3-one (XI), 22,29,30-trisnorlupan-3,19-dione (XII), 22,29,30-trisnorlupana-3,12-dione (XIII), lupeol-TMS (XIV), lup-22(29)-en-3-on-29-ol-TMS (XV), 22,29-epoxy-29-lupan-13-one (XVI), lup-3-on-29-al (XVII), lup-3-on-29-ol-TMS (XVIII), 19, 22-epoxy-29-lupan-3-one (XIX), friedelin (XX), 4-epi-friedelin (XXI) and AO (tris(2,4-di-tertbutylphenyl) phosphate). (AO was detected in most of the extracts due to some contamination from plastic materials during the experiment).](image-url)
procedure as mentioned above. The TICs showing the distributions of the transformation products and precursor compounds are presented in Fig. 1. Structural identification was based on the MS fragmentation pattern of the transformation products and on comparison with published data. No transformation product was detected for friedelin (XX; Fig. 1c and d). This may due to the stability of friedelin to this oxidation condition.

3.1. Transformation products of β-amyrin

The details of the transformation products identified from the ozonation experiments are given in Table 1. For β-amyrin, 7 transformation products were identified. The main reactions in the ozonation of β-amyrin were found to occur at ring C and these results are different from the photochemical and microbial alteration of triterpenoids where most of the reactions occur at ring A (Corbet et al., 1980; Simonet et al., 2009).

The mass spectra and key ions for compound identification are presented in Fig. SI-1 (Supplementary information). The peak for β-amyrin–TMS (I) with the molecular ion at m/z 498 appears at 42.08 min (Fig. 1a) and matches the standard. For the transformation products, the peak at the retention time of 44.39 min is attributed to the TMS derivative of 12,13-epoxyolean-3β-ol (III). This compound with a base peak at m/z 234 shows the presence of an epoxy group at C-12 to C-13 of β-amyrin (Fig. SI-1a). The peaks at 45.90 and 46.26 min are attributed to 11-oxo-olean-12-en-3β-ol (VI) and 12-oxo-olean-3β-ol (VII), respectively. The molecular ion of 11-oxo-olean-12-en-3β-ol–TMS (VI) is at m/z 512 with loss of TMS to m/z 440 and two significant fragments at m/z 234 and m/z 205 (Fig. SI-1b), the latter ions indicating the presence of a ketone group at C-11 as well as a double bond at C-12 to C-13. The mass spectrum of 12-oxo-olean-3β-ol–TMS (VII) has a base peak at m/z 189, two key ions at m/z 234 and m/z 219 and M+ at m/z 514 (Fig. SI-1c). This fragmentation pattern indicates the presence of a ketone group at C-12.

The mass spectra for the peaks at 44.50 and 45.31 min are attributed to the TMS derivatives of 8,14-seco-olean-14-en-3β-ol (IV) or 8,14-seco-olean-13-en-3β-ol (V) that form by cleavage of the C-8 to C-14 bond of 12-oxo-olean-3β-ol. The mass spectra of these two compounds have similar fragmentation patterns with a peak at m/z 73 indicating the presence of a TMS group on the C-3β OH, a rearrangement fragment at m/z 234 supporting the presence of ketone group at C-12, and the base peak at the m/z 189 for the ring D/E fragment (Fig. SI-1d). Therefore, the structures were assigned as shown (IV or V). The peak at 46.50 min is attributed to the TMS derivatives of 8,14-seco-olean-3,12-dione (VIII) that form by cleavage of the C-8 to C-14 bond of 12-oxo-oleanan-3-one. The mass spectrum for compound VIII has the molecular ion at m/z 442 with no fragments at m/z 73 or m/z 514 supporting a ketone functionality at C-3 (Fig. SI-1e). In addition, the ions m/z 207 and m/z 234 represent cleavage of the C-9 to C-11 bond. Based on review of the literature, all compounds identified, except β-amyrone, have not been reported elsewhere and thus are tentative interpretations.

3.2. Transformation products of lupene

For lupene, the 10 transformation products identified are listed in Table 2 and shown in Fig. 1b as the TIC. The mass spectra and key ions for compound identification are shown in Fig. SI-2. The main reactions in the ozonation of lupene occur at the isopropenyl group attached to ring E. Based on the GC–MS analysis, the peak at 42.26 min is lupene (IX). The mass spectra of the peaks at 38.78 and 39.45 min are attributed to 22,29,30-trisnorlup-18(19)-en-3-one (X) and 22,29,30-trisnorlupan-3-one (XI), respectively (Fig. SI-2a and b). These two compounds formed by the elimination of the isopropenyl group from lupene. The mass spectra exhibit similar fragmentation patterns, with molecular ion, M-CH3, ring A/B fragment at m/z 205 and ions at m/z 147 and m/z 149 for X and XI, respectively. The presence of m/z 147 in the mass spectrum of X indicates one double bond in ring E.

The peaks at 42.90 and 43.30 min are interpreted as 22,29,30-trisnorlupan-3,19-dione (XII) and 22,29,30-trisnorlupan-3,12-dione (XIII), respectively. Both XII and XIII formed by incorporation of a ketone group at C-9 and C-12, respectively, and also have similar mass spectra (Fig. SI-2c and d). The major difference between these two compounds is the presence of m/z 149 in the MS of XIII, which indicates that the additional ketone group is not at ring E.

The peak at 44.74 min is a mixture of lupeol (XIV) and lupan-3-one and their mass spectra match those of the standards. Lupeol has been frequently reported in plant extracts (Chaturvedi et al., 2008) and some geochemical studies (Simonet, 2008). The mass spectrum of the peak at 45.66 min fits for lup-22(29)-en-3-29-ol (XV) as the TMS derivative (Fig. SI-2e). The intense m/z 422 fragment indicates the loss of TMSOH from C-29. The peak for lupan-3-29-ol–TMS (XVIII) appears at 47.88 min and the MS has the molecular ion at m/z 514 indicating the presence of the monohydroxylated isopropyl group, and the intense ion at m/z 411 is from the elimination of CH3OTMS (Fig. SI-2f).

The mass spectra for the peaks at 46.38 and 47.10 min have similar fragmentation patterns (Fig. SI-2g). The loss of C5H9O from M+ to m/z 382 represents the side chain at ring E indicating the additional oxygen atom on the isopropyl group of lupene. Thus, these two mass spectra are interpreted to be 19,22-epoxylupan-3-one (XVI) or lupan-3-29-ol (XVII), respectively. The mass spectrum of the peak at 48.55 min represents another epoxidized derivative of lupene. The fragment at m/z 205 supports the presence of an oxygen atom on the isopropyl group, with further elimination of methyl to m/z 191 (Fig. SI-2h). This is interpreted to be 19,22-epoxylupan-3-one (XIX).

3.3. Mechanisms for the transformation of triterpenoids by ozonation

3.3.1. β-Amyrin

During ozonation, β-amyrin can react with O3 and OH. However, the mechanisms for the transformation of β-amyrin were proposed mainly based on the reaction with OH since the transformation products that can be produced from the reaction with O3 through the Criegee mechanism (Criegee, 1975) were not detected. The reaction between O3 and β-amyrin is expected to form sec0-compounds through the breakdown of the double bond at C-12 to C-13 as indicated by the Criegee mechanism (Hasson et al., 2003). Based on the

Table 1

<table>
<thead>
<tr>
<th>Compoundsab</th>
<th>Retention time (min)</th>
<th>Composition</th>
<th>Molecular weight</th>
<th>M+</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Amyrin (I)</td>
<td>42.08</td>
<td>C30H46O4</td>
<td>426</td>
<td>498</td>
</tr>
<tr>
<td>β-Amyrone (II)</td>
<td>41.67</td>
<td>C30H46O4</td>
<td>424</td>
<td>424</td>
</tr>
<tr>
<td>12,13-Epoxyoleanan-3β-ol (III)</td>
<td>44.39</td>
<td>C30H46O4</td>
<td>442</td>
<td>514</td>
</tr>
<tr>
<td>8,14-seco-12-oxooleanan-3β-ol (IV)</td>
<td>44.50</td>
<td>C30H46O4</td>
<td>442</td>
<td>514</td>
</tr>
<tr>
<td>8,14-seco-12-oxooleanan-3β-ol (V)</td>
<td>45.31</td>
<td>C30H46O4</td>
<td>442</td>
<td>514</td>
</tr>
<tr>
<td>11-Oxo-oleanan-12-en-3β-ol (VI)</td>
<td>44.50</td>
<td>C30H46O4</td>
<td>442</td>
<td>514</td>
</tr>
<tr>
<td>12-Oxo-oleanan-3β-ol (VII)</td>
<td>45.90</td>
<td>C30H46O4</td>
<td>440</td>
<td>512</td>
</tr>
<tr>
<td>8,14-seco-oleanan-3,12-dione (VIII)</td>
<td>46.26</td>
<td>C30H46O4</td>
<td>442</td>
<td>442</td>
</tr>
</tbody>
</table>

a Compounds containing a hydroxyl group are analyzed as TMS derivatives in GC–MS.

b Roman numerals refer to structures in Appendix A.
transformation by products, the reactions have occurred at the double bond at C-12 to C-13, the hydroxyl group attached to C-3, and the bond at C-8 to C-14. For the reaction at the double bond at C-12 to C-13, the mechanism is proposed to start from the initial attack of \( /C5\)OH that was generated from the decomposition of O3 in water, on \(-\)amyrin to form radical \( B\) (Fig. 2a). Derivatives \( III\) with epoxy groups could form by the reaction of \( B\) with \( OH\) through pathway \( A2\). Radical \( B\) could also react with water and \( OH\) to form compound \( VII\) as indicated by pathway \( A1\). The ring C opening is proposed to start from hydrogen abstraction at C-15 by \( /C5\)OH to form radical \( C\) as indicated by pathway \( A3\). Radicals \( B\) could also react with water and \( /C5\)OH to form compound \( V\) as indicated by pathway \( A1\). The ring C opening is proposed to start from hydrogen abstraction at C-15 by \( /C5\)OH to form radical \( C\) as indicated by pathway \( A3\). Radicals \( D\) further reacts with water to form seco-compound \( IV\). Double bond migration occurs by further reaction with \( /C5\)OH to form \( V\). The formation of \( VI\) starts by hydrogen abstraction at C-11 to form radical \( E\) (pathway \( A4\), Fig. 2b). Radical \( E\) then reacts with \( /C5\)OH to form mono-hydroxylated \(-\)amyrin, \( F\), which further reacts with \( OH\) to form radical \( G\). Intramolecular rearrangement of \( G\) leads to the formation of \( V\). The formation of \(-\)amyrone (\( II\)) is proposed to start from hydrogen abstraction by \( OH\) at the C-3 hydroxyl group followed by the intramolecular elimination of \( H\) with \( OH\) (pathway \( A5\)).

### Table 2
Details of the identified transformation products from lupenone.

<table>
<thead>
<tr>
<th>Compounds (^a)</th>
<th>Retention ( t) (min)</th>
<th>Composition</th>
<th>Molecular weight</th>
<th>( M^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lupenone (IX)</td>
<td>42.26</td>
<td>( C_{30}H_{48}O )</td>
<td>424</td>
<td>424</td>
</tr>
<tr>
<td>22,29,30-Trisnorlupen-18(19)-en-3-one (X)</td>
<td>39.45</td>
<td>( C_{27}H_{42}O )</td>
<td>382</td>
<td>384</td>
</tr>
<tr>
<td>22,29,30-Trisnorlupan-3-one (XI)</td>
<td>42.90</td>
<td>( C_{27}H_{42}O_2 )</td>
<td>398</td>
<td>398</td>
</tr>
<tr>
<td>22,29,30-Trisnorlupan-3,19-dione (XII)</td>
<td>43.30</td>
<td>( C_{27}H_{42}O_2 )</td>
<td>398</td>
<td>398</td>
</tr>
<tr>
<td>Lupeol (XIV)</td>
<td>44.74</td>
<td>( C_{30}H_{48}O )</td>
<td>426</td>
<td>498</td>
</tr>
<tr>
<td>Lup-19(22)-en-3-on-29-ol (XV) (^a)</td>
<td>45.66</td>
<td>( C_{30}H_{48}O_2 )</td>
<td>440</td>
<td>512</td>
</tr>
<tr>
<td>22,29-Epoxylupan-3-one (XVI)</td>
<td>46.38 or</td>
<td>( C_{30}H_{48}O_2 )</td>
<td>440</td>
<td>440</td>
</tr>
<tr>
<td>Lupan-3-on-29-al (XVII)</td>
<td>47.10</td>
<td>( C_{30}H_{48}O_2 )</td>
<td>440</td>
<td>440</td>
</tr>
<tr>
<td>Lupan-3-on-29-ol (XVIII) (^a)</td>
<td>47.88</td>
<td>( C_{30}H_{48}O_2 )</td>
<td>442</td>
<td>514</td>
</tr>
<tr>
<td>19,22-Epoxylupan-3-one (XIX)</td>
<td>48.55</td>
<td>( C_{30}H_{48}O_2 )</td>
<td>440</td>
<td>440</td>
</tr>
</tbody>
</table>

\(^a\) Compounds containing a hydroxyl group are analyzed as TMS derivatives in GC–MS. 
\(^b\) Roman numerals refer to structures in Appendix A.

#### 3.3.2. Lupenone

The reactions for lupenone occur mainly at the isopropenyl group where the double bond is located (Fig. 3). As \(-\)amyrin, the transformation products based on the reaction between O3 and lupenone were not detected. The mechanism of lupenone degradation is proposed to start from the initial attack of \( /C5\)OH on lupenone to form radical \( J\), which is the precursor for the formation of \( XVIII, XV, XI\) and \( X\) (Fig. 3a). Intermediate \( J\) can react with \( /C5\)OH to form \( XVI\) (pathway \( L1\)). On the other hand, \( J\) can also react with water and undergo intramolecular rearrangement to form \( XVIII\) (pathway \( L2\)) and \( XV\) (pathway \( L3\)), respectively. Rearrangement of \( J\) through the elimination of the 1-hydroxypropyl carbanion forms radical \( K\) (pathway \( L4\)).
Fig. 3. Mechanisms for the transformation of lupenone in ozonation to (a) 22,29,30-trisnorlup-18(19)-en-3-one (X), 22,29,30-trisnorlupan-3-one (XI), 22,29,30-trisnorlupana-3,19-dione (XII), lup-22(29)-en-3-on-29-ol (XV), 22,29-epoxylupan-3-one (XVI), lupan-3-on-29-al (XVII) and lupan-3-on-29-ol (XVIII), (b) 19,22-epoxylupan-3-one (XIX) and lupeol (XIV), and (c) 22,29,30-trisnorlupana-3,12-dione (XIII).
As radical J, radical K can also react with water and undergo intramolecular rearrangement to form X, XI and XII (pathways L4.1, L4.2 and L4.3, respectively). The formation of XVII is proposed to start with the reaction between XVIII and "OH to form radical L (pathway L2.1), followed by elimination of a hydrogen radical to form XVII.

The formation of XIX commences with hydrogen abstraction by "OH at C-19 of lupenone to form radical M (Fig. 3b, pathway L5) and further intramolecular rearrangement and reaction with water to form intermediate N. Subsequent reaction of N with "OH yields intermediate O, which rearranges to form XIX. Lupeol (XIV) could form from reaction of the ketone group at C-3 with "OH to the hydroperoxide P (pathway L6), whose instability leads to the elimination of "OOH to form radical Q. Then reaction of Q with water forms XIX. The formation of XIII is as the case for β-amyrin, and it can be produced from XI through a similar pathway (Fig. 3c).

4. Conclusion

Characterization of the transformation products formed during ozonation of β-amyrin, lupenone and friedelin was performed using GC–MS. The experiments produced various derivatives from β-amy-}

Appendix A

Chemical structures of compounds cited in the text.
Appendix B. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orggeochem.2013.01.001.

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