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Instructions for use

Hydroxyl radical-induced photochemical formation of dicarboxylic acids from

unsaturated fatty acid (oleic acid) in aqueous solution

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Abstract

In this study, we assess under laboratory controlled conditions the direct and hydroxyl radical ($\cdot$OH)-induced photochemical production of low molecular weight (LMW) dicarboxylic acids and related compounds (C_2-C_9) (DCAs) from oleic acid (*cis*-9-octadecenoic, $\Delta 9C_{18}$) in aqueous solution. Nitrate (NO_3^-)-amended and unamended oleate solutions were irradiated under ultraviolet-B radiation (UV-B, 313 nm) for 5 h, with NO_3^- being the source of $\cdot$OH. The $\cdot$OH-induced photochemical production of DCAs (C_{2di}-C_{9di}) (165 ± 32 nM h^{-1}) was much higher than that induced by the direct effect of UV-B (33 ± 31 nM h^{-1}), accounting for 85% of the total (direct + $\cdot$OH-induced) photochemical production of DCAs (C_{2di}-C_{9di}) (194 ± 6 nM h^{-1}). Azelaic acid (C_{9di}) was the dominant photoproduct (comprising 63 and 44% of DCAs in the direct and $\cdot$OH-induced photochemical production, respectively) followed by C_{8di}, C_{7di} and C_{6di}, whereas shorter chain compounds (C_{2di}-C_{5di}) were minor produced species. Using our estimate of $\cdot$OH photoproduction (P-OH in nM h^{-1}), the production of C_{9di} from 50 μM of oleic acid was evaluated to ~ 36 nM (nM $\cdot$OH)$^{-1}$. We propose in this work a chemical mechanism for the reaction of $\cdot$OH with oleic acid in aqueous solution from the cleavage of its double bond, and the subsequent formation of DCAs through oxidation and decarboxylation processes.

Keywords: Oleic acid; dicarboxylic acids; hydroxyl radical; nitrate; UV-B radiation

1. Introduction

Low molecular weight (LMW) dicarboxylic acids and related compounds (C_2-C_9) (DCAs) are ubiquitous water soluble organic compounds that have been detected in a variety of environmental samples including atmospheric aerosols [1], rain waters [2], ice cores [3], marine sediments [4], fresh waters [5] and seawater [6]. Because of their hygroscopic properties, DCAs can act as cloud condensation nuclei and have an impact on the radiative forcing at the Earth's surface [7]. In atmospheric aerosols, one of the major sources of DCAs is direct and sensitized photooxidation of unsaturated hydrocarbons and fatty acids [8,9,10]. Sensitized photooxidation is initiated by powerful oxidizing agents such as ozone (O_3), hydroxyl radical (OH) and nitrate radical (NO_3), which are produced by the interactions between ultraviolet-B radiation (UV-B: 280-315 nm) and volatile organic compounds and nitrogen oxides.

The reaction of oleic acid (*cis*-9-octadecenoic, $9C_{18}$) with O_3, OH and NO_3 has recently emerged as a model system to better understand the photooxidation processes affecting unsaturated fatty acids in atmospheric aerosols [11,12]. Oleic acid is degraded through an oxidative cleavage of its double bond to produce C_9 compounds, i.e., nonanoic (C_9), 9-oxononanoic (ωC_9) azelaic (C_{9di}) acids and 1-nonanal (C_{9ald}) [13,14,15,16] as well as nitrated carboxylic acids [12]. Secondary photooxidation reactions could initiate the production of lower molecular weight DCAs such as C_{2di}-C_{8di} [9,17,18]. Although the production of DCAs from photooxidation of unsaturated fatty acids has been largely studied in the atmospheric aerosols, little is known about the direct and sensitized photoproduction of DCAs in aqueous solutions. In seawater, it has been shown that oleic acid, which is produced by phytoplankton [19], was directly photooxidized to produce ωC_9 and C_{9ald} [20]. However, there is no report of concentrations of a homologous series of DCAs from these

photooxidation processes. In natural waters, many photochemical reactions are driven by OH, which is one of the most reactive oxidants (E = +1.83 V) [21,22,23]. Major sources of OH in natural waters are the nitrate (NO_3^-) and nitrite (NO_2^-) photolysis, initiated by UV-B and UV-A (315-400 nm), respectively, as well as the photolysis of colored dissolved organic matter (CDOM), initiated by both UV-B and UV-A [24,25,26]. Photochemical oxidation reactions may substantially modify molecular distribution and bacterial availability of dissolved organic compounds in natural waters and then play a significant role in aquatic carbon cycle [27,28].

The objective of this study is to assess under laboratory controlled conditions the direct and OH-induced photochemical production of DCAs from oleic acid in aqueous solution (pure water). NO_3^- was chosen as photosensitizer and source of OH radicals since **(i)** quantum yield of OH formation (Φ_{OH}) from NO_3^- photolysis is well known [25,26,29], **(ii)** NO_3^- is very poor OH scavenger (k < 1.10^5 s^{-1}) compared to NO_2^- (k = 1.10^{10} s^{-1}) in aqueous solutions [25] and **(iii)** in natural waters NO_3^- is often found in much higher concentrations than NO_2^-. The production of OH from the UV-B photolysis of NO_3^- is described by the equations [30,31]:

$$[NO_3^- + \textit{UV-B} \rightarrow NO_3^-]^* \qquad\qquad (1)$$

$$[NO_3^-]^* \rightarrow NO_2 + O^- \qquad\qquad (2)$$

$$O^- + H_2O \rightarrow OH + OH^- \qquad\qquad (3)$$

2. Materials and methods

2.1. Irradiation experiment

Sodium oleate (99% purity, Sigma, 50 μM final concentration) was added to 0.2-μm filtered Milli-Q water (final resistivity > 18 MΩ cm^{-1}). The pH of Milli-Q water was 6 before adding oleate and 7.6 after the dissolution. To stimulate the production of OH, a subsample of the oleate solution was amended with NO_3^- (Fluka, 15 μM final concentration). The NO_3^--amended and unamended oleate solutions were then dispensed into precombusted (450°C for 6 h) quartz and glass (Pyrex) tubes (100 ml volume) that were sealed with ultraclean (extensively rinsed with 1 N HCl and Milli-Q water) silicone stoppers wrapped in Teflon foil. The tubes were irradiated for 5 h under two UV-B fluorescent lamps emitting mainly at 313 nm (Q-Panel UVB-313, 40W) at controlled room temperature (15 ± 1°C). Quartz tubes, which were used for the UV-B condition, were wrapped in 95 μm cellulose diacetate filter to remove residual UV-C (200-280 nm) of the lamps (Fig. 1). Pyrex tubes were wrapped in aluminum foil for the dark controls. Duplicate samples were exposed for each light/NO_3^- treatment. Subsamples for DCA analysis were collected before (T0) and after (T5) 5-h irradiation and stored in 250-ml precombusted glass bottles poisoned with $HgCl_2$ (10 mg l^{-1} final concentration) at 4°C in the dark until measurements.

Irradiance of the UV-B lamps was measured with a IL-1700 broadband radiometer (International Light) equipped with a UV-B probe (SUD240, International Light) covered by cellulose diacetate filter. Irradiance received by the samples was controlled by the distance between lamps and tubes. It was fixed at 4.10^{-5} W cm^{-2}, which approximately corresponds to a natural UV-B irradiance at solar noon in summer in mid-latitudes. Irradiance integrated over 5-h irradiation was $7.45 \cdot 10^{-1}$ J cm^{-2}.

2.2. Measurement of dicarboxylic acids and related compounds

DCAs were measured by gas chromatography and flame ionization detection (GC/FID) after butyl ester derivatization [32]. The sample (50 ml) was first concentrated down to 3-4 ml using a rotary evaporator under a vacuum, then transferred into a 25 ml pear-shaped flask, further concentrated by the rotary evaporator and finally concentrated to almost dryness under a nitrogen stream. A total of 0.25 ml of 14% BF_3/n-butanol was immediately added to the sample and the flask was sealed with a glass stopper, Teflon tape and clamp. The organic acids and reagent were mixed under ultrasonication for 1 min and then heated at 100°C for 30 min to derive dibutyl esters for carboxyl group and dibutoxy acetal for aldehyde group. The derivatives were extracted with 5 ml of *n*-hexane after adding 3 ml of Milli-Q water and 0.2 ml of acetonitrile. The hexane layer was further washed with Milli-Q water (3 × 3 ml). The esters were dried by using a rotary evaporator, then a nitrogen stream and were finally dissolved in 100 μl of *n*-hexane prior to GC/FID determination. The dibutyl esters were determined with a Hewlett Packard 5890 gas chromatograph equipped with a split/splitless injector, a fused silica capillary column (HP-5, 25 m × 0.32 mm × 0.52 μm) and an FID detector. Peak identification was performed by a comparison of GC retention times with those of dibutyl ester standards.

2.3. Assessment of OH photoproduction

OH photoproduction (P-OH) from the UV-B irradiation of 15 μM NO_3^- was assessed using the following photochemical equation:

$$P\text{-}OH(313) = E_0(313) \times a(313) \times \Phi_{OH}(313) \qquad (4)$$

Where P-OH(313) is production of OH at 313 nm (in nM h^{-1}), $E_0(313)$ is irradiance received by the samples at 313 nm (4.10^{-5} W cm^{-2} which corresponds to 0.0072 mol photon m^{-2} h^{-1}), a(313) is absorption coefficient of 15 μM NO_3^- at 313 nm (0.027 m^{-1}; Fig. 2) and $\Phi_{OH}(313)$ is quantum yield of OH formation from NO_3^- photolysis at 313 nm used from [29] (1.3% at

20°C and pH 6.2-8.2) that we corrected by temperature effect according to the following formula [33]:

$$\Phi_{OH}(288\ K) = \Phi_{OH}(298\ K)\ exp\ [(1800 \pm 480)\ (1/298 - 1/288)] \qquad (5)$$

The value of $\Phi_{OH}(313)$ we used for 15°C was 1.05%. Consequently, P-OH in the NO_3^--amended oleate solutions exposed to UV-B was estimated to be ~ 2 nM h^{-1}.

3. Results and Discussion

Table 1 presents the concentrations of DCAs (C_{2di}-C_{9di}, ωC_9) detected in the oleate solutions before and after 5-h irradiation. We observed that the total concentration of DCAs after irradiation under UV-B in the presence of NO_3^- (T5 UV-B + NO_3^-) (1140 ± 30 nM) was much higher than that under UV-B alone (T5 UV-B) (314 ± 156 nM) (Table 1). 9-oxononanoic acid (ωC_9) was not detected in the different samples, whereas azelaic acid (C_{9di}) was found as the dominant species, accounting for ~ 36% and 42% of the total DCA concentration in conditions T5 UV-B and T5 UV-B + NO_3^-, respectively (Table 1). These concentrations are closed to that found recently in Mediterranean surface seawater samples (700-730 nM) [6].

In order to evaluate the photochemical production of DCAs (in nM h^{-1}) from the 5-h irradiation of oleic acid, the concentrations reported in Table 1 for UV-B conditions were corrected for the corresponding "dark" and then divided by a factor 5. Direct (UV-B-induced), OH-induced and total (direct + OH-induced) photochemical productions of DCA were determined by subtracting the DCA concentration in UV-B by that in dark ([DCA]$_{T5\ UV-B}$ - [DCA]$_{T5\ dark}$), the DCA concentration in UV-B + NO_3^- by that in UV-B ([DCA]$_{T5\ UV-B + NO3-}$ - [DCA]$_{T5\ UV-B}$) and the DCA concentration in UV-B + NO_3^- by that in dark + NO_3^- ([DCA]$_{T5\ UV-B + NO3-}$ - [DCA]$_{T5\ dark\ +\ NO3-}$), respectively. The photochemical productions of each DCA were then summing to obtain the photochemical production of total DCAs (C_{2di}-C_{9di}) (Fig. 3).

Clearly, the ·OH-induced photochemical production of DCAs (165 ± 32 nM h^{-1}) was much higher than that induced by the direct effect of UV-B (33 ± 31 nM h^{-1}), accounting for 85% of the total (direct + ·OH-induced) photochemical production of DCAs (194 ± 6 nM h^{-1}) (Fig. 3). Consequently, the UV-B photolysis of NO$_3^-$ and the subsequent production of ·OH (P-OH $\sim$ 2 nM h^{-1}) and its reaction with oleic acid is much more efficient in producing DCAs (from C$_{9di}$ to C$_{2di}$) than the direct effect of UV-B on oleic acid, the latter leading only to the production of DCAs from C$_{9di}$ to C$_{7di}$ (Fig. 3). C$_{9di}$ was the dominant photoproduct (comprising 63 and 44% of DCAs in the direct and ·OH-induced photochemical production, respectively) followed by C$_{8di}$, C$_{7di}$ and C$_{6di}$, whereas shorter chain compounds (C$_{2di}$-C$_{5di}$) were minor species (·OH-induced production) or not detected as photoproducts (direct production) (Fig. 3). The ·OH-induced photochemical degradation of oleic acid led to a C$_{9di}$ production of 72 ± 16 nM h^{-1} (Fig. 3). Therefore, using our P-OH calculated value of 2 nM h^{-1}, the production of C$_{9di}$ from 50 μM of oleic acid in aqueous solution can be assessed to $\sim$ 36 nM (nM ·OH)$^{-1}$.

The total photochemical production of DCAs (C$_{2di}$-C$_{9di}$) for 5-h irradiation (971 nM) represents 7.4 μM C and thus account for 0.8% of the initial concentration of oleic acid (900 μM C). In addition to DCAs (C$_{2di}$-C$_{9di}$), many other intermediates and photochemically stable compounds are likely produced from the ·OH-induced degradation of oleic acid in aqueous solution. For atmospheric aerosols, some authors reported the photoproduction of C$_9$, ωC$_9$, C$_{9di}$ and C$_{9ald}$, as well as nitrated carboxylic acids from the reaction of oleic acid with ·OH, O$_3$ or NO$_3$ [12,13,14,15,16]. In this study, C$_9$ and C$_{9ald}$ could not be determined using our GC/FID technique. However, ωC$_9$ was found to be below the detection limit in the samples, suggesting that this compound, once produced from oleic acid, was immediately oxidized into C$_{9di}$.

A chemical mechanism for the reaction of ·OH radicals with oleic acid in aqueous solution and the subsequent formation of DCAs (C$_{2di}$-C$_{9di}$) is proposed in Figure 4. Both the

action of ˙OH that is produced by the UV-B photolysis of NO_3^-, and dissolved oxygen (O_2) in the aqueous solution, leads to the cleavage of the double bond of oleic acid and to the production of two C_9 compounds, i.e., ωC_9 and C_{9ald}. From the action of both $^\bullet OH$ and O_2, ωC_9 is oxidized into C_{9di}. The oxidation of DCAs is assumed occurring via H-atom abstraction by ˙OH followed by the O_2-induced formation of peroxy radical. From C_{9di}, other DCAs (C_{8di} to C_{2di}) are then produced through oxidation and decarboxylation processes involving the formation of hydroxy diacid, keto diacid, ωketoacid and diacid (C_{n-1di}).

This study clearly shows that ˙OH efficiently produces DCAs, especially C_{9di}, from unsaturated fatty acids in aqueous solution. As regard to the experimental conditions we used, including pH, temperature, irradiance as well as NO_3^- and oleate concentrations, we can expect to have, qualitatively, similar C_{2di}-C_{9di} photochemical production in various natural waters including fresh, river and rain waters. However, in seawater, ˙OH, which reacts almost exclusively with bromide ion (Br^-) to generate the less reactive dibromide anion ($Br_2^{\bullet-}$), is unlikely as efficient in degrading unsaturated fatty acids [22,34].

Acknowledgments

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Figure legends

Figure 1. Transmittance of light via cellulose diacetate filter.

Figure 2. UV absorption spectrum of 15 µM NO_3^- in Milli-Q water measured using a Shimadzu UV-1605 spectrophotometer equipped with a 10-cm quartz cuvette.


Figure 3. Direct ($[DCA]_{T5\ UV-B}$ - $[DCA]_{T5\ dark}$), OH-induced ($[DCA]_{T5\ UV-B\ +\ NO3-}$ - $[DCA]_{T5\ UV-B}$) and total (direct + OH-induced) ($[DCA]_{T5\ UV-B\ +\ NO3-}$ - $[DCA]_{T5\ dark\ +\ NO3-}$) photochemical production of DCAs (C_{2di}-C_{9di}) (in nM h^{-1}) from UV-B irradiation of 50 µM oleic acid in aqueous solution.

Figure 4. Proposed chemical mechanism for the reaction of OH with oleic acid in aqueous solution and the subsequent formation of DCAs (C_{2di}-C_{9di}) through oxidation and decarboxylation processes.

Table I. Concentrations (in nM) of dicarboxylic acids (C_{2di}-C_{9di}) and oxocarboxylic acid (ωC_9) in the NO_3^--amended and unamended oleate solutions before (T0) and after (T5) 5-h irradiation under UV-B lamps or in the dark.
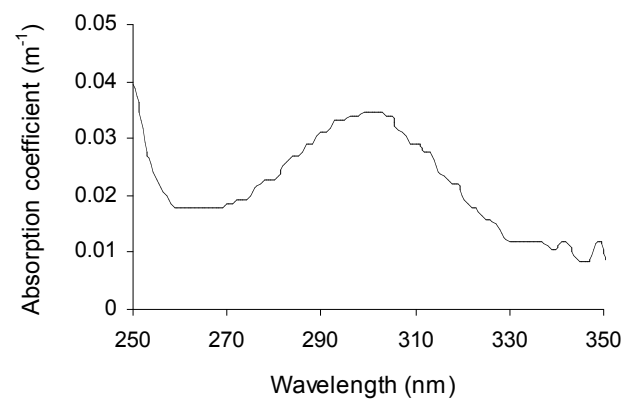
compounds	T0	T0 + NO_3^-	T5 dark	T5 dark + NO_3^-	T5 UV-B	T5 UV-B + NO_3^-
oxalic acid, C_{2di}	25	41	33 ± 15	27 ± 6	23 ± 7	60 ± 5
malonic acid, C_{3di}	14	9	18 ± 21	8 ± 4	5 ± 1	39 ± 1
succinic acid, C_{4di}	14	11	7 ± 0	10 ± 0	8 ± 1	31 ± 7
glutaric acid, C_{5di}	10	2	2 ± 2	3 ± 4	2 ± 1	24 ± 35
adipic acid, C_{6di}	116	102	97 ± 4	92 ± 6	72 ± 14	198 ± 38
pimelic acid, C_{7di}	30	22	10 ± 8	6 ± 4	27 ± 32	156 ± 42
suberic acid, C_{8di}	31	25	21 ± 20	9 ± 6	63 ± 68	156 ± 30
azelaic acid, C_{9di}	37	39	11 ± 2	14 ± 1	114 ± 75	476 ± 30
9-oxononanoic, ωC_9	0	0	0	0	0	0
Total	277	251	199 ± 7	169 ± 5	314 ± 156	1140 ± 30

For T5 conditions, averaged concentrations are given with a standard deviation based on duplicate samples exposed in the same light/NO_3^- conditions.
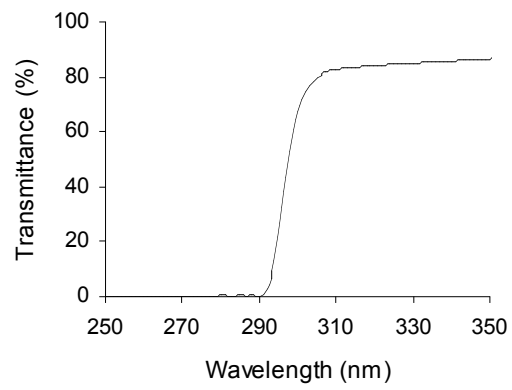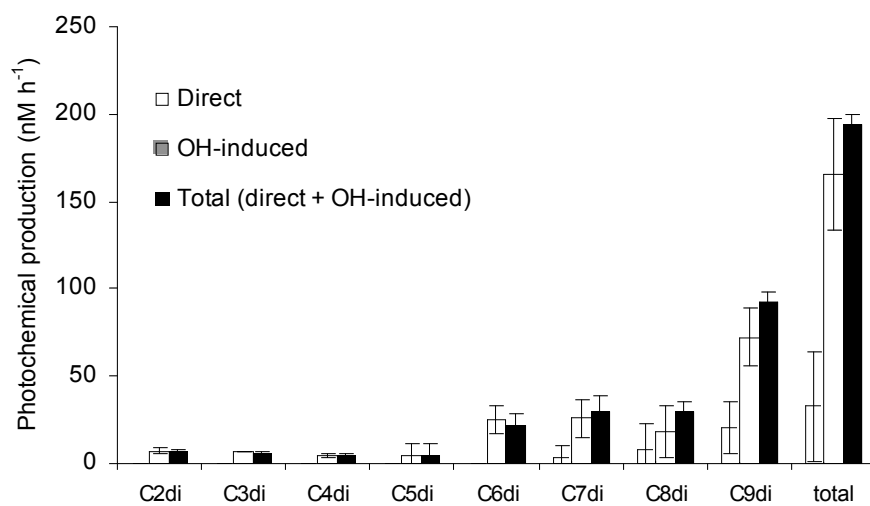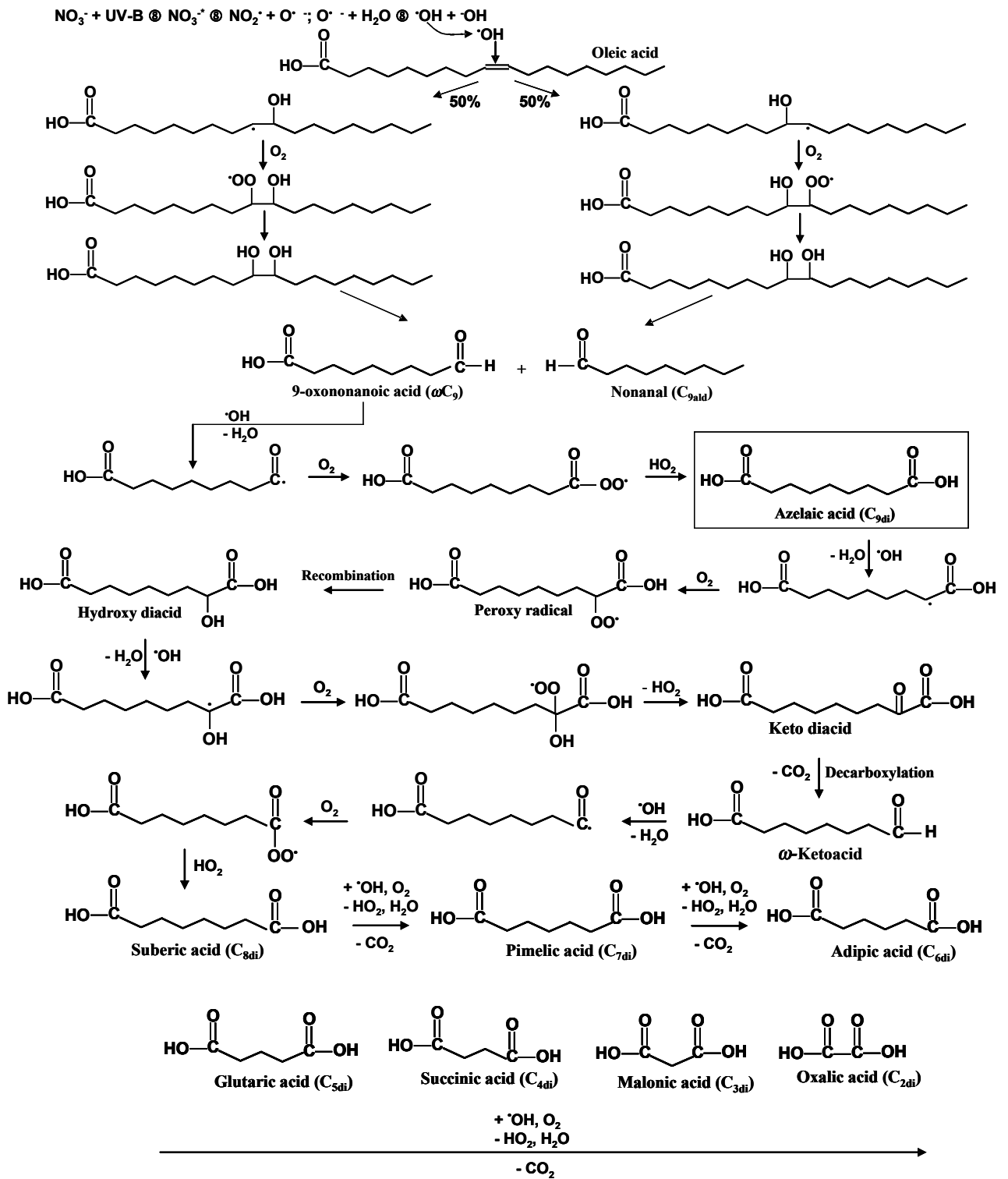
Figure 1

Figure 2

Figure 3

Figure 4