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Dedicated to the greatest scientist and my respected mentor Omarov Rustem

Toxicity of reactive carbonyl compounds to plants

Abstract. *In plants, environmental stresses result in oxidative stress, lipid peroxidation and the generation of reactive carbonyl aldehydes. Reactive carbonyl aldehydes are downstream products of reactive oxygen species which can be described as critical cell-damaging agents in plants under various environmental stresses. In this paper toxicity of reactive carbonyl aldehydes and its generation under stress conditions are discussed. Moreover, involvement of reactive carbonyl aldehydes in stress- induced damage to plants is demonstrated. Toxic effect of reactive aldehydes such as acrolein, malondialdehyde and crotonaldehyde in plants under different stresses and their high electrophilicity is also discussed. Increases in malondialdehyde was demonstrated in UV-C stressed plants as the result of carbonyl modified proteins. A malondialdehyde is one of the widely shown aldehyde, which can be demonstrated as an indicator of reactive oxygen species. Malondialdehyde isomerized to 3-hydroxyacrolein whereas it can be described as a dialdehyde. The article considers detrimental actions of reactive carbonyl aldehydes and their chemical properties as well as detoxification of reactive carbonyl aldehydes by multiple enzymes such as aldehyde dehydrogenase, aldehyde reductase, aldo-keto reductase and 2-alkenal reductase.*
Keywords: *reactive carbonyl aldehydes, reactive oxygen species, lipid hydroperoxide, toxicity, malondialdehyde.*

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Formation of reactive carbonyl aldehydes under environmental stresses

Plants are constantly exposed to environmental stresses, such as extreme temperatures, drought and salinity and lead to a rise in the level of reactive oxygen species (ROS) in cells (Asada, 2006; Mano et al., 2019). Further, ROS oxidizes lipids to form lipid peroxides (LOOHs) and LOOHs undergo oxidative degradation to generate reactive carbonyl aldehydes (RCA) (Blée, 1998; Mano, 2012) (Fig.1). RCA are downstream products of ROS, which can be generated in plants under normal physiological conditions, and their level increases under stress conditions. The accumulation of carbonyls in excess can be very toxic, because they may mediate the oxidative injury of plants. (Biswas and Mano, 2016; Srivastava et al., 2017). The involvement of RCA in such stress- induced damage to plants was previously reported by different studies. Increased level of α,β-unsaturated aldehydes which are considered to be strong electrophiles (Esterbauer et al.,1991) was observed in tobacco leaves under photo inhibitory illumination (Mano et al., 2010). Additionally, the toxic effect of aldehydes was observed in tobacco roots exposed to aluminum treatment (Yin et al., 2010). Increases in malondialdehyde (MDA), acrolein and crotonaldehyde were shown in heat and salt stressed plants as the result of carbonyl modified proteins (Yamauchi et al., 2008; Mano et al., 2014). Moreover, the involvement of carbonyls in plant cell death induced by hydrogen peroxide and salt stress was also reported (Biswas and Mano, 2015). Recently, it was revealed that an enhanced level of aldehydes can induce silique senescence in aldehyde oxidase 4 mutant in *Arabidopsis thaliana* under different stresses (Srivastava et al., 2017).

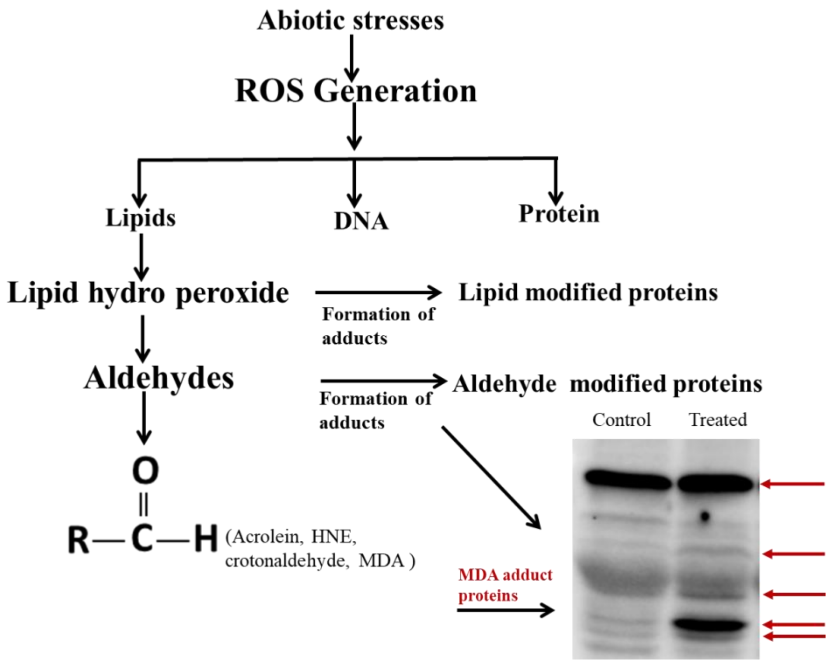

Figure 1. Schematic pathway generation of toxic aldehydes under abiotic stresses. Red arrows indicate increases in the MDA modification level of SDS-PAGE fractionated *Arabidopsis* leaf proteins 3 days after UV-C stress application as compared to control (unstressed) proteins

Toxicity of RCA

There is an increasing body of evidence for the toxicity of aldehydes in plants (Mano et al., 2002; Mano, 2012; Biswas and Mano, 2015; Srivastava et al., 2017). Among lipid peroxide derived carbonyls, *α*, β-unsaturated aldehydes such as hydroxy-2-nonenal HNE, acrolein and crotonaldehyde were identified as the most reactive species. Due to this reactivity, they may exert cytotoxicity at low levels while less reactive aldehydes such as formaldehyde and MDA can be toxic only at much higher levels (Esterbauer et al.,1991). In plants HNE can inhibit mitochondrial enzymes such as decarboxylating dehydrogenases (Millar and Leaver, 2000) and alternative oxidases, which are directly involved in the inhibition of the mitochondrial electron transport (Winger et al., 2005). Moreover, HNE, acrolein and *trans*-2-hexanal can inhibit photosynthesis in the chloroplasts and acrolein can affect the Calvin cycle enzymes. The involvement of crotonaldehyde in the inactivation of CO2-photoreduction was observed as well (Mano et al., 2009). Cell injury and retardation in growth of roots was also observed as a result of accumulated aldehydes such as HNE, acrolein, MDA and formaldehyde under aluminum treatment (Yin et al., 2010). Increased level of MDA and its damaging effect was observed under different stresses such as chilling or UV-B (Hodgson and Raison, 1991; Panagopoulos et al., 1992). Acrolein, which is one of the most toxic products of LOOH, can induce plant cell death by the activation of Caspase-3-Like Proteases (Biswas and Mano, 2016). Additionally, it was shown that methyl viologen treatment can cause severe damage to plants due to enhanced acrolein and crotonaldehyde accumulation (Yamauchi et al., 2012). Modification of proteins with RCA such as acrolein, crotonaldehyde, HNE, HHE and MDA can cause irreversible damage to plants (Mano et al., 2014). The toxic effect of exogenously applied aldehydes such as acrolein, HNE, benzaldehyde and hexanal was demonstrated to cause early senescence in siliques (Srivastava et al., 2017). The involvement of RCA in lateral root formation and the toxic effect of aldehydes such as 3-Z-hexanal, n-hexanal was also shown to result in the accumulation of anthocyanins, bleaching in leaves, and retardation of root growth (Biswas et al., 2019). Thus, it is well established that detoxification of carbonyl aldehydes is essential for maintaining plants viability.

Detoxification of RCA by enzymes

Detoxification of aldehydes was attributed to enzymes such as aldehyde dehydrogenase (ALDH; EC 1.2.1.3) that oxidizes aldehydes to the corresponding carboxylic acids using NAD or $NAD(P)^+$ as coenzymes(Sunkar et al., 2003; Stiti et al., 2011; Widhalm and Dudareva, 2015), aldo-keto reductase (AKR; EC 1.1.1.2) and aldehyde reductase (ALR; EC 1.1.1.2) that reduces the carbonyl groups to alcohols by using NADPH as an electron donor (Oberschall et al., 2000; Yamauchi et al., 2011), 2-alkenal reductases (AER, EC 1.3.1.74) that reduce double bond of carbonyls to saturated aldehydes (Mano et al., 2002), glutathione transferase tau isozymes (GST) that also contribute to detoxification of RCS in plants (Mano et al., 2019a) (Figure 2). Recently, it was shown that aldehyde oxidase 4, mainly expressed in silique, but not in leaves, can catalyze the detoxification of aldehydes resulting in the delay of siliques senescence in *Arabidopsis* (Srivastava et al., 2017).

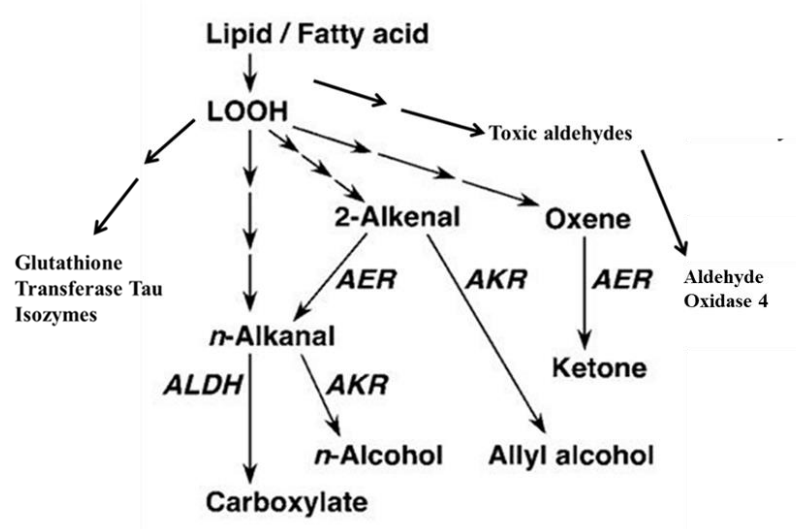

Figure 2. Pathway of detoxification of lipid peroxide-derived reactive carbonyl aldehydes in plants. Enzyme abbreviations are as follows: AER, Alkenal reductase; AKR, aldo-keto reductase; and ALDH, aldehyde dehydrogenase, Modified from Mano et al.

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Реактивті карбонил қосылыстарының өсімдікке улылығы

Аңдатпа. Өсімдіктерде қоршаған ортаның стресстері тотығу стрессіне, липидтердің асқын тотығуына және реактивті карбонил альдегидтерінің түзілуіне әкеледі. Реактивті карбонил альдегидтері әртүрлі экологиялық стресстер кезінде өсімдіктерде жасушаны зақымдайтын маңызды агенттер ретінде сипаттауға болатын реактивті оттегі түрлерінің төменгі ағынындағы өнімдері болып табылады. Бұл жұмыста реактивті карбонил альдегидтерінің уыттылығы және оның стресс жағдайында түзілуі талқыланады. Сонымен қатар, реактивті карбонил альдегидтерінің өсімдіктердің стресстен туындаған зақымдалуына қатысуы көрсетілген. Сондай-ақ, акролеин, малондиальдегид және кротональдегид сияқты реактивті альдегидтердің өсімдіктерге әртүрлі кернеулер кезінде токсикалық әсері және олардың жоғары электрофильділігі талқыланады. Карбонилді түрлендірілген белоктардың нәтижесінде УК-С стресске ұшыраған өсімдіктерде малондиальдегидтің жоғарылауы көрсетілді. Өйткені, малондиальдегид реактивті оттегі түрлерінің көрсеткіші ретінде көрсетуге болатын кең таралған альдегидтердің бірі болып табылады. Малондиальдегид 3-гидроксиакролеинге дейін изомерленген, ал оны диальдегид ретінде сипаттауға болады. Маңыздысы, реактивті карбонил альдегидтерінің зиянды әрекеттері және олардың химиялық қасиеттері, сондай-ақ альдегиддегидрогеназа, альдегидредуктаза, альдо-кеторедуктаза және 2-алкеналды редуктаза сияқты көптеген ферменттер арқылы реактивті карбонил альдегидтерін детоксикациялау да талқыланады.

Түйін сөздер: реактивті карбонил альдегидтер, реактивті оттегі түрлері, липидтердің гидропероксиді, уыттылық, малондиальдегид.

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Токсичность реактивных карбонильных соединений для растений

Аннотация. У растений стрессы окружающей среды приводят к окислительному стрессу, перекисному окислению липидов и образованию реактивных карбонилальдегидов. Реактивные карбонилальдегиды - это продукты, находящиеся ниже по потоку от активных форм кислорода, которые можно охарактеризовать как критические агенты, повреждающие клетки растений при различных стрессах окружающей среды. В статье обсуждаются токсичность реакционноспособных карбонилальдегидов и ее образование в стрессовых условиях. Кроме того, продемонстрировано участие реактивных карбонилальдегидов в стресс-индуцированном повреждении растений. Обсуждаются токсическое действие реактивных альдегидов, таких как акролеин, малоновый диальдегид и кротоновый альдегид, на растения при различных стрессах и их высокая электрофильность. Повышение уровня малонового диальдегида было белков, модифицированных карбонилом. Поскольку малоновый диальдегид является одним из широко используемых альдегидов, который можно продемонстрировать как индикатор продемонстрировано у растений, подвергшихся воздействию УФ-С, в результате применения

активных форм кислорода. Малоновый диальдегид изомеризован в 3-гидроксиакролеин, тогда как его можно описать как диальдегид. Важно отметить, что также обсуждаются пагубное действие реакционноспособных карбонилальдегидов и их химические свойства, а также детоксикация реакционноспособных карбонилальдегидов множеством ферментов, таких как альдегид дегидрогеназа, альдегид редуктаза, альдокеторедуктаза и 2-алкеналредуктаза.

Ключевые слова: реактивные карбонилальдегиды, активные формы кислорода, гидропероксид липидов, токсичность, малоновый диальдегид.

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