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Non-Enzymatic Antioxidants in Stressed Plants: A Review

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A R T I C L E   I N F O

A B S T R A C T

Plants are exposed to different ecological stress during their life cycle, and because of these tensions, free radicals are shaped. Reactive oxygen species(ROS) have a fundamental ability to support typical plant improvement and stress tolerance. The disruption of the proportionality of ROS generation and antioxidant defense systems is one of the primary effects of biotic and abiotic stress, resulting in an excess of ROS buildup and oxidative damage in plants. Plants may combat this issue by producing ROS-neutralizing compounds, and both enzymatic and non-enzymatic antioxidant defense mechanisms maintain the proper ratio between ROS generation and detoxification. Ascorbic acid (AsA), glutathione (GSH), flavonoids, Vitamin E (α-tocopherols), and carotenoids are crucial non-enzymatic antioxidants in this context, with a high potential for performing a variety of crucial activities in plants under both stressful and unstressful conditions, in addition to scavenging ROS. This review illustrates the main roles of some non-enzymatic antioxidants in plants subjected to various types of biotic and abiotic stresses.

Introduction:

It is generally acknowledged that a deeper comprehension of plant tissue and organ development is necessary for enhancing agricultural output and production. Both external environmental conditions and genetic programming have an impact on plant body. Abiotic (such as salinity, light and dark, temperature, nutrition and water availability, and harmful compounds like heavy metals) and biotic (such as helpful and pathogenic microbes, fungus, insects, and other herbivores) interactions all have a role in the environment that plants thrive in [1]. Reactive oxygen species (ROS) and reactive nitrogen species (RNS), also known as excess amounts of molecules containing activated oxygen, are to blame for this, which led to oxidative damage. Despite being reactive and hence detrimental, ROS and RNS are essential components of

signal transduction pathways that start stress reactions. Additionally, ROS and RNS contribute to the growth of plants [2]. Plant ROS are byproducts of aerobic metabolism that are created in a number of cellular organelles, including chloroplasts [3], mitochondria [4], and peroxisomes [5].

Plants generate a huge number of ROS species that control a range of functions, including defense against pathogen, programmed cell death (PCD), and stomatal activity, when the environment is unfavorable[6].

Additionally, Nawkar et al. [7] showed that NADPH oxidases and peroxidases can enhance the production of ROS. These responses typically result in aberrant plant growth or death because they have severe or permanent impacts on tissue and organ development. Additionally, ROS controls plant growth and stress responses through interacting with hormones and epigenetic modifiers [8]. Several key biological processes, such as cellular differentiation and proliferation, require low levels of ROS to proceed [9]. At higher concentrations, ROS represent a serious

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concern that might ultimately result in DNA deterioration and erroneous PCD timing. Under typical conditions, these molecules mediate the signaling transduction response in plant cells [10]. However, under stress conditions, ROS, such as hydrogen peroxide, are well known for causing cellular damage, toxicity, and photosynthesis suppression [11]. As a major plant defense mechanism against a range of stress circumstances, massive ROS accumulation and scavenging are crucial mechanisms that facilitate more effective ROS consumption (biotic or abiotic). The ROS-scavenging system has drawn the greatest interest. Enzymes such as SOD and CAT as well as from the ascorbate-glutathione cycle, such as monodehydroascorbate reductase (MDAR), ascorbate peroxidase (APX), dehydroascorbate reductase (DHAR), and glutathione reductase (GR), are part of this process. Nonenzymatic components include ascorbate, glutathione, α-tocopherols, and carotenoids [12]. Increased antioxidant defense, according to multiple studies, fights oxidative damage brought on by abiotic stressors such as drought, salt , floods, heat , cold, heavy metal toxicity, ozone, and UV rays [13]. It is possible for plants to acquire opioid tolerance to abiotic stressors by developing plants with higher antioxidant capacity.

This review outlines the function of non-enzymatic antioxidants that expose plant systems to various stresses and make them more tolerant to these extreme conditions.

Oxidative Stress and Free Radicals in Plants:

ROS includes both free radicals "radicals of superoxide anion ($O^{\bullet-}_2$), hydroxyl radicals ($OH^\bullet$), perhydroxyl radicals ($HO_2^{\bullet-}$), organic peroxyl radicals ($ROO^\bullet$) , organic alkoxy radicals ($RO^\bullet$), and non-radical (molecular) forms such as hydrogen peroxide (H_2O_2), singlet oxygen ($^1O_2$) ,and ozone (O_3) "[14]. The generation of ROS is disrupted by increased environmental stresses, reducing the antioxidants' activity and resulting in oxidative damage. Reactive oxygen species are formed as a result of the highly common redox reactions (electronic exchanges between a donor and an acceptor) in living creatures [15]. Because plants have an effective defensive system that keeps the proper balance between ROS production and elimination, redox homeostasis emerges in plant cells as

a result of the equilibrium between ROS formation and antioxidant action [16]. A basal level of ROS that is kept above the cytostatic or below the cytotoxic concentration is necessary for appropriate ROS or redox transmission in cells, and so this level is maintained by the equilibrium of ROS generation and ROS elimination [17]. As a result, scientists began referring to ROS as chemical messengers that maintain and manage plants' regular physiological processes under the umbrella of "redox biology" [18]. Redox signaling is the balance between low ROS levels that serve as signals to start taken on greater that change typical plant activities and excessive levels of ROS that cause oxidative cell injury [19]. As a result of, cellular redox-sensitive components cooperate with ROS generation and ROS scavenging systems to shape and subtly alter downstream signaling pathways in a cell and context-specific manner spanning time and space [20]. Under the influence of a variety of abiotic stress conditions, any disruption in the equilibrium of ROS generation and ROS scavenging by antioxidants causes ROS excess accumulation and oxidative stress [21]. Lipid peroxidation due to oxidative stress, which is thought to be caused by OH⁻ ions reacting with all DNA constituents, damaging purines, pyrimidines, and proteins and altering glucose metabolism, ultimately leading to cell failure and death (Figure 1) [10].
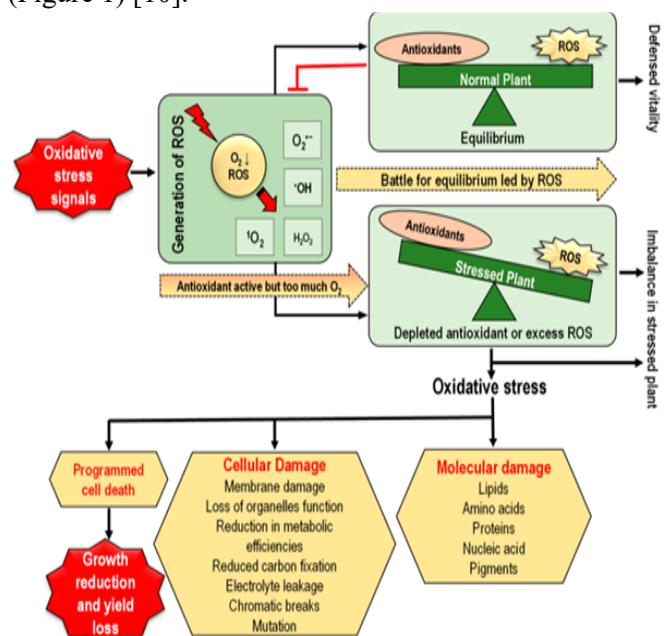

Figure 1 : Plant oxidative stress and its repercussions ROS; $^1O_2$; $O_2^{\bullet-}$; H_2O_2 and $^\bullet OH$ [19].

Plant Protection with Antioxidants:

Plant antioxidants act as a natural storage facility for bioactive compounds. They are necessary for plant adaptability to environmental challenges, but they are also beneficial to human health. Plants, as stationary organisms, cannot avoid natural or man-made environmental challenges (e.g., temperature (hot or cold), water availability (drought or flooding), soil composition, light intensity, day/night rhythms, pests, habitat damage, pollution, radiation, etc.) that cause oxidative stress by upsetting the balance between the production and scavenging of ROS [13]. Although ROS are necessary for healthy plant growth and development as well as signal transmission, they may potentially harm cells [10]. Maintaining the oxidative equilibrium is thus critical for plant stress tolerance. As shown in Table 1, xanthine oxidase, peroxidases (PODs), lipoxygenases oxidase, and reduced nicotinamide adenine dinucleotide phosphate hydrogen (NADPH) are among the enzymes involved in the iron-catalyzed Fenton reaction [22] that causes oxidative stress in plants. The outcome of the plant under oxidative stress depends on the balance between ROS and antioxidative capability. On the other hand, diverse and cooperative ROS-scavenging antioxidant mechanisms that change the intracellular ROS concentration strictly control increased ROS formation.

Table 1: Reactive oxygen species in plant cells: types, reactivity, production locations, and scavenging mechanisms [22].

ROS	The ROS sign (+/−)	Reactivity	Production sites	System of scavenging	
				Enzymatic	Non-enzymatic
Hydrogen peroxide	H_2O_2, nonradical	interacts with heme proteins, proteins that contain cysteine and methionine residues, and DNA.	Peroxisomes, chloroplasts, mitochondria, cytosol, and apoplasts are all examples of organelles.	CAT, APX, PER, GPX, PRX, GSH	Ascorbate
Hydroxyl radical	$OH^{\bullet}$, radical	DNA, RNA, lipids, and proteins are all highly reactive macromolecules.	Fenton reaction include Iron, H_2O_2		Sugars, flavonoids, proline, ascorbate
Singlet oxygen	$^1O_2$, nonradical	Oxidation occurs in lipids, proteins (Trp, His, Tyr, Met, and Cys residues), and DNA G residues.	Membranes, chloroplasts, nucleus		α-tocophero ,Carotenoids
Superoxide	$O_2^{\bullet-}$, radical	It dismutates into H_2O_2 when it interacts with Fe-S proteins.	Chloroplasts, mitochondria, peroxisomes, apoplasts (RBOHs), and electron transport chains	SOD	Ascorbate ,flavonoids

- Ascorbate peroxidase (APX), catalase (CAT), glutathione (GPX), glutathione (GSH), peroxidase (PER), peroxiredoxin (PRX), and respiratory burst oxidase (RBOH).

It is helpful to divide these processes into enzymatic and non-enzymatic antioxidants. Under typical circumstances, the antioxidant defense system protects against active oxygen and free radicals. The response becomes moderate or poor, however, when the equilibrium between ROS production and scavenging is disrupted by stressful conditions [23]. "Antioxidant enzymes such as SOD, CAT, POX, polyphenol oxidase (PPO), APX, MDHAR, DHAR, GR, GPX, GST, TRX, and PRX interact with nonenzymatic antioxidants such as AsA, GSH, α-tocopherol, flavonoids, alkaloids, and nonprotein amino acids to prevent excessive ROS production" [24] Figure (2). Plants' greater tolerance to abiotic stress is thought to be linked to the fast removal of excess ROS [25]. These ROS-dependent signals and reactions govern the overall response of the plant cell to the specific conditions.
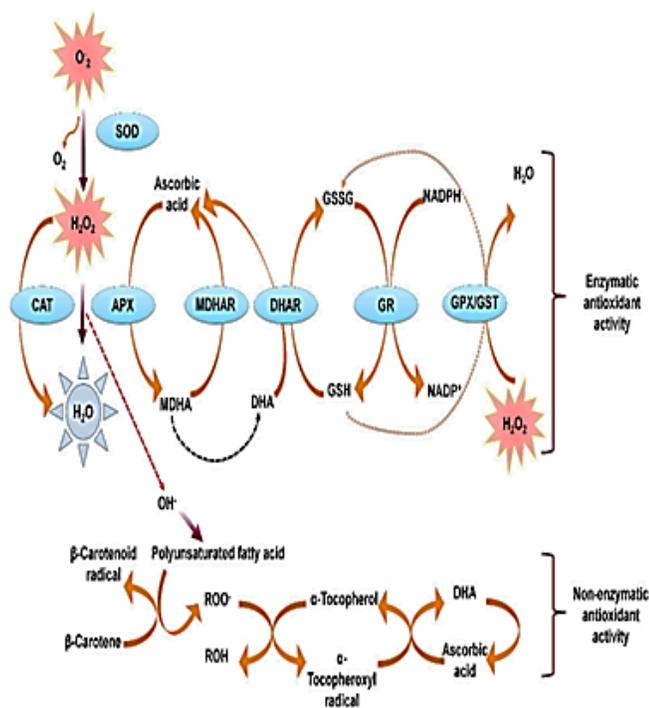

Figure 2: Reactive oxygen species (ROS) are detoxified by plant cells through enzymatic antioxidant and nonenzymatic oxidant activities. "Superoxide dismutase (SOD), catalase (CAT), ascorbic peroxidase (APX), glutathione peroxidase (GPX), and glutathione S-transferase(GST), MDHA reductases (MDHARs) and DHA reductases (DHARs) and glutathione reductase are examples of antioxidant enzymes . Examples of non-enzymatic antioxidant activity necessary for ROS removal include reduced glutathione (GSH), β-carotene (vitamin A), Ascorbic acid (vitamin C), α-tocopherol (vitamin E)". [26].

Plants' Non-Enzymatic Antioxidants:

Reactive oxygen species (ROS) are detoxified by plant cells through enzymatic antioxidant and nonenzymatic antioxidant activities. Glutathione, ascorbic acid, α-tocopherol, proline, carotenoids, flavonoids, and glutathione are examples of non-enzyme low molecular mass substances. The mechanism of action of these molecules is based on altering the metabolic function of the cell with the intention of stabilizing membranes by interacting with polyunsaturated acyl groups of lipids, protecting versus ROS produced during photosynthetic and respiratory processes, and cooperating with other antioxidants [27]. Nonenzymatic antioxidants are more common than enzymatic antioxidants [23].

Non-enzymatic antioxidants include the following:
1. Ascorbic acid (Vitamin C) or AsA   2. Glutathione (GSH)   3. Flavonoids
4. Vitamin E (α-tocopherols)   5. Carotenoids (Car)
All of these compounds aid plants by scavenging ROS.

1- Ascorbic acid (Vitamin C) or AsA

Ascorbate, often known as vitamin C, is necessary for humans, and a shortage in it can result in a number of harmful conditions, including scurvy[28]. Ascorbic acid is a vitamin C truncated form derived from hexose sugar. Chemically, there are three isomeric forms of vitamin C: L-ascorbic acid is the most widely utilized of the three ascorbic acids, along with D-arabo-ascorbic acid and L-arabo-ascorbic acid. Almost all kinds of higher plant are capable of producing ascorbic acid, but only animals that are able to oxidize L-gulono-1,4-lactone are able to do so. There are three main biosynthetic pathways that plants use to make ascorbic acid. The cell's specialization and metabolic regulation determine fluxes through distinct routes. Vitamin C is well known for its Antioxidant qualities, which help to protect plants from oxidative damage. Its involvement in how plants react to various kinds of stimuli, including salt, drought, heat and cold stress, metal, and, more lately, ozone stress, has been proven. Ascorbic acid (ASC) is required for plant reactions to stress. Despite substantial study into ASC's antioxidant activity,

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regarding the function of ASC in plants' reaction to abiotic stress, there are still a number of unanswered concerns [29].

ASC may scavenge ROS, which should assist plants in coping with stress. However, in other cases, increasing ASC concentration diminishes plant tolerance to abiotic stress. However, lowering ASC synthesis or regeneration increases a plant's ability to withstand stress. This fascinating observation suggests that ASC may have roles other than antioxidant in plants' response to abiotic stress [30]. Numerous case studies have shown a connection between increased expression and increased stress tolerance. Furthermore, stress-tolerant genotypes had higher endogenous ascorbic acid levels, showing that it is required in stressed cells. ASC effectively neutralizes accumulated ROS via either direct or indirect ways in its role as an antioxidant, making it necessary for preventing oxidative injury and enhancing plant resistance to abiotic and biotic stresses [31]. "ASC has antioxidant characteristics, but it may also function as a cofactor for certain oxides, such as 2-oxoglutarated dioxygenases (2-ODDs), and it may aid in the production of a number of plant hormones [32]. It functions as a cofactor for the enzymes aminocyclopropane-1-carboxylic acid oxidases (ACOs) and 9-cis-epoxycarotenoid dioxygenases (NCEDs)", both of which are necessary for the synthesis of the agonist hormones (ABA) and ethylene [33]. Plant responses to biotic and abiotic stresses are regulated by phytohormones. As a result, ASC helps plants respond to abiotic stress via pathways of phytohormones [34]. Furthermore, as a coenzyme, it contributes to epigenetic alteration and influences plant responses to abiotic stress via nongenetic influence pathways [35].

It is necessary for plants to maintain intracellular and extracellular redox balances [36]. Redox homeostasis in plants affects a number of communication circuits, such as the ROS, ABA, and auxin signal transduction pathways, and contributes to the transmission of stress signals [34]. Plants can successfully scavenge a variety of ROS, both directly and indirectly, and so maintain cellular redox equilibrium [32]. The ability of ROS to be scavenged and plant stress tolerance can both be markedly improved by increasing the ASC concentration as a result of its enhanced production [37]. As a result, ASC

plays a critical role in the removal of oxidative stress and the improvement of tolerance for abiotic stress. ROS are produced as a result of a sequence of redox reactions that are started by photosynthesis. In chloroplasts, one of the most significant locations for the creation of reactive oxygen species, chlorophyll (chl) and light interact to create reactive oxygen species[38].

The principal ROS sources in this instance are the triplet chl chain, which includes PSI and PSII, and electron transport chain (ETC) carriers. In chloroplasts, ASC scavenges both radical and nonradical ROS, enhancing plant photosynthesis.Under stressful conditions, SOD facilitates the removal of O_2 by dismutating it into O_2 and H_2O. H_2O_2 is broken down by the CAT into water and oxygen. To remove H_2O_2, POX works in the extracellular space. Plants' GPX catalyzes the transformation of H_2O_2 and HO_2 into lipid alcohols and water. GR catalyzes the conversion of oxidized glutathione (GSSG; dimeric) to reduced glutathione (GSH; monomeric). Ascorbate is a specific electron donor used by APX to convert H_2O_2 to water, whereas ASC acts as an electron source [39]. On the other hand, inhibiting ASC de novo production significantly reduces plant stress resistance. Plants need to regenerate ascorbate through the ASC recycling route to reduce ROS harm and boost their resistance to abiotic stress [40]. By oxidizing agents ASC to monodehydroascorbate (MDHA), APXs can effectively scavenge ROS. Then MDHA can be excessively converted to DHA and ASC [41]. ASC may be regenerated from MDHA and DHA by MDHA and DHA reductases, respectively. In this situation, ASC regeneration can contribute more ASC for ROS shielding, preserving cellular redox balance, and reducing oxidative injury in the face of abiotic stress [37]. Ascorbate contributes electrons to the AsA-GSH cycle and maintains its stability due to electron delocalization brought on by the resonance among two types [42], as seen in Figure 3. Ascorbic acid (AsA) is also a regenerant α-tocopherol (vitamin E), capable of scavenging $OH^{\bullet}$ and $O^{\bullet-}_2$, as well as tocopheroxyl radicals [43].

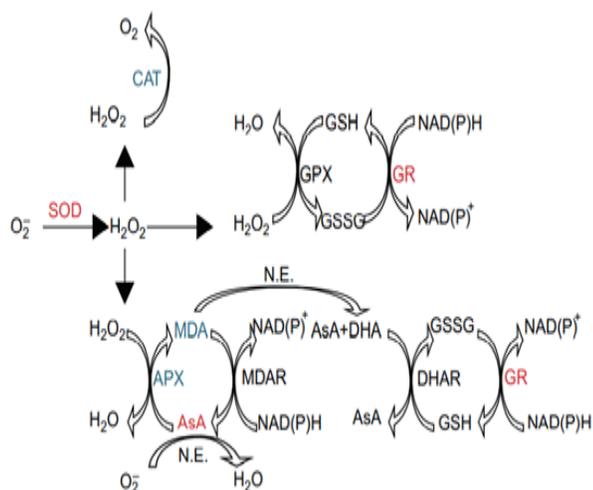*Journal of University of Anbar for Pure Science (JUAPS)*   Open Access


Figure 3: Ascorbate-glutathione cycle and some other metabolisms for scavenging ROS [42].

2-Glutathione (GSH)

Strong antioxidant glutathione detoxifies ROS and shields plants from oxidative damage[44]. Numerous functions, such as cell formation, pathogen resistance, enzymatic regulation, senescence, and cell death, depend on glutathione. Reduced glutathione (GSH) serves as an efficient antioxidant by assisting in the elimination of reactive oxygen free radicals brought on by stress. Each and every cell compartment, such as the cytosolic, chloroplasts, endoplasmic reticulum, vacuoles, and mitochondria, contains the tripeptide glutathione (gamma-glutamyl-cysteinylglycine). Additionally, GSH helps to detoxify organic pollutants and functions as a reduced sulfur storage and transportation form [45]. Glutathione production is based on two sequential amino acid reactions [46]"The first step in glutathione biosynthesis is the production of γ-glutamylcysteine." γ - glutamylcysteine synthetase (γ -ECS, GSH1) catalyzes the reaction of L-glutamate with L-cysteine, releasing energy as adenosine triphosphate (ATP)". The carboxyl group of glutamate and the amino group of cysteine combine to create a peptide bond. The addition of glycine to γ-glutamylcysteine is the next step. The N-terminus of glycine and the C-terminus of γ-glutamylcysteine are connected by a peptide. The enzyme that catalyzes the formation of glutathione(GS, GSH-S, GSH2) is called glutathione synthetase . The procedure also needs adenosine triphosphate (ATP). GSH2 enzyme is primarily present in the cytosol, whereas the GSH1 enzyme regulates glutathione

synthesis and is normally found in plastids [47]. There are two forms of this antioxidant that may be found in plants: reduced disulfide (GSH) and oxidation disulfide (GSSG) [44].
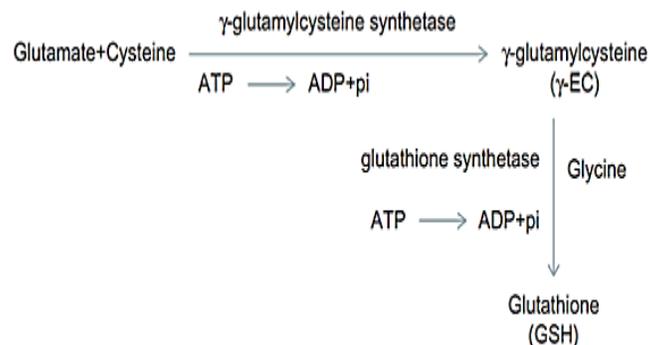

In ideal circumstances, leaves have a GSH/GSSG ratio greater than 20:1. A large percentage of these forms (the GSH/GSSG ratio) must be preserved to inactivate the inhibitory activity of ROS-induced oxidative stress [46]. It may accelerate the reducing of GSSG to GSH, such as in the ascorbate-glutathione cycle, and can scavenge H2O2, 1O2, and the most dangerous ROS, such as OH$^{\cdot}$. GSH may be generated in plant chloroplasts and cytoplasm or via glutathione reductase (GR), utilizing NADPH as a donor electron. [48]. GSH functions as an ambient redox sensor stimuli. According to recent research, increasing GSH levels improves resistance to diverse abiotic stressors [49]. GSH can be used as a stress indicator in the system of antioxidant defense because of where it is located. Different redox signaling pathways depend on the proportion of H_2O_2 reduced (GSH) to oxidation (GSSG) during decomposition [50]. Glutathione helps transgenic Arabidopsis plants tolerate drought stress, as discovered by Chen et al. [51].

3-Flavonoids

Low-molecular-weight flavonoids, in particular dihydroxy B-ring replaced flavones and flavonols, are highly effective at removing free radicals and defending cells from peroxidation[52]. Flavonoids are metabolites formed from plants that serve a number of purposes, such as defense and signaling during stress. These compounds encompass a wide range of chemical subunits, with flavonols being one of the most prevalent [53]. As important as they are, a key class of polyphenols found throughout the plant world comprise a broad group of secondary or specialized plant

metabolites (PSMs) that are either constitutively generated or activated by environmental stimuli [54]. Two aromatic rings (A and B) joined by units of three carbons (the C ring), which might or might not give rise to a third aromatic ring, make up the basic 15-carbon atom structure C6-C3-C6 of flavonoids [55]. They fall under a variety of classifications, including "Chalcones, Aurones, Flavanonols, Flavones, Isoflavones, Flavanols, Flavonols, Anthocyanins, Proanthocyanidins, and Leucoanthocyanidins. Aglycones, glycosides, and methylated derivatives of flavonoids are found in nature. There have already been identified more than 6000 distinct flavonoids" [56].

Numerous physiological roles have been given to flavonols. Recent studies have shown that flavonoids can protect indigenous Mediterranean species against UV and dehydration stress. Abiotic stresses also activated antioxidative mechanisms and enhanced the expression of genes involved in the synthesis of flavonoids [57]. Quercetin and myricetin are among the most researched flavonoid sub-groups due to the catechol molecule in the flavonol's B-ring [58]. As the most effective antioxidant substances and crucial elements in plants' adaptations to climate change, flavonols may indirectly regulate plant development. Primary rationale for flavonols' antioxidant activity is the strong the subsequent reaction [59] demonstrates the reactivity of their hydroxyl substituents:

$$R^{\bullet} + F\text{-}OH \rightarrow RH + F\text{-}O^{\bullet}$$
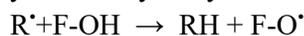
The ability of flavonoids to donate electrons or hydrogen ions makes them powerful antioxidants. They work as antioxidants through a variety of processes. As described in the preceding response, first is direct ROS scavenging. Metal chelation also prevents ROS formation. Quercetin, for example, has a significant propensity to chelate metal ions such as Fe and Cu ions, thereby reducing the generation of free radicals, including harmful ROS [60]. Flavonols can create metal flavonol complexes due to their distinct structures, particularly the groups of hydroxyl [61]. They may also limit the activity of enzymes that produce free radicals, including glutathione S-transferase and NADH oxidase, as well as perhaps activate antioxidant enzymes that have the ability to scavenge radicals [62].

4- Vitamin E (α-tocopherols)

α-Tocopherols (Vitamin E) are lipophillic antioxidants found in all plants' green portions. They scavenge lipid-peroxy radicals during the intense activities of other antioxidants, which are only produced by photosynthetic organisms such as plants, algae, and the majority of cyanobacteria [63]. Plants' α-tocopherol synthesis is genetically controlled and stimulated by oxidative stress . Tocopherol levels in plant tissues range from extremely low (1 mg/g dry weight) to highly high (10 mg/g dry weight). Tocopherol concentration varies between species and among tissues within the same plant, ranging from an elevated concentration (1 g/g dry weight) in leaves and seeds to incredibly low amounts (0.1 g/g dry weight) in roots and stems [64]." In general, leaf α-tocopherol accumulates, despite the fact that seeds are high in γ-tocopherol [65]. The levels of β- and δ-tocopherols are low in the majority of plant species. α-tocopherol is synthesized in chloroplasts in the plastid envelopes from γ-tocopherol by γ-tocopherolmethyltransferase (γ-TMT) and stored in chloroplast stroma, plastoglobuli, and thylakoid membranes [66]. They have a polar chromanol ring made of homogentisate (HGA) and a lipophilic isoprenoid side chain made from a specific prenyl pyrophosphate donor" [67].

Condensation of HGA with PPP initiates the output of tocopherol, which is arbitrated by homogentisate phytyl transferase (*VTE2*) and leads to the formation of 2-methyl-6-phytyl-1,4-benzoquinol (MPBQ). The tocopherol biosynthesis route has been well categorized in recent years, with all the vitamin E biosynthetic genes (*VTE* genes) involved [68] as clear in Figure 4. "Following this step, the route can split into two branches, resulting in the synthesis of β- and δ-tocopherol or α- and γ-tocopherol, depending on MPBQ's subsequent response. An MPBQ methyltransferase (MPBQMT; *VTE3*) or δ- tocopherol cyclase(TC; *VTE1*) can then either immediately cyclize the MPBQ or methylate it into 2,3-dimethyl-6-phytyl-1,4-benzoquinol (DMPBQ) . DMPBQ, the end product, is then changed by the aforementioned TC (*VTE1*) into γ-tocopherol   The last step in the production of tocopherol is the methylation of β- and α-tocopherol and γ-tocopherol, which is performed by the enzyme γ-tocopherol methyltransferase (γ-TMT; *VTE4*). Because MPBQ-MT (*VTE3*), TC (*VTE1*), and γ-TMT (*VTE4*)

also are engaged in the synthesis of the other tocochromanols, only HPT (*VTE2*) is considered unique to tocopherol synthesis. These steps make up the tocopherol-core pathway" [68].
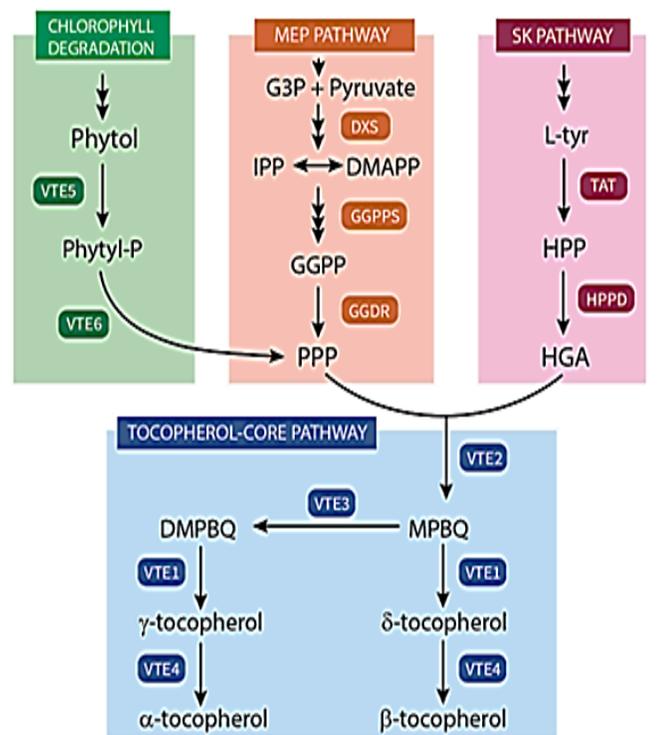

Figure 4: Tocopherol biosynthesis route in plants is depicted schematically. "Phytyl-P, phytyl phosphate; PPP, phytyl pyrophosphate; DMAPP, dimethylallyl diphosphate; L-Tyr, amino acid L-tyrosine; IPP, isopentenyl diphosphate; G3P, glyceraldehyde 3-phosphate ; HPP, 4-hydroxyphenylpyruvate; HGA, homogentisate;GGPP, geranylgeranyl diphosphate; DMPBQ, 2,3-dimethyl-6-phytyl-1,4-benzoquinol; MPBQ, 2-methyl-6-phytyl-1,4-benzoquinol; *VTE2*, homogentisate phytyltransferase (HPT); *VTE1*, tocopherol cyclase (TC); *VTE5*, phytol kinase; *VTE6*, phytyl-P kinase; DXS, 1-deoxy-D-xylulose-5-phosphate synthase; GGPPS, GGPP synthase; GGDR, GGPP reductase; TAT, tyrosine aminotransferase; *VTE3*, MPBQ methyltransferase (MPBQ-MT); HPPD, HPP dioxygenase; *VTE4*, tocopherol methyltransferase (γ-TMT)" [67].

Along with removing reactive oxygen species like singlet oxygen, their antioxidant effect is connected to the reduction of reactive oxygen species and the prevention of breakdown of membrane lipids [69]. Its primary function is to offer tolerance against abiotic challenges, while transgenic experiments have shown that it can also provide tolerance to plants in biotic stress

[66]. Mutant Arabidopsis plants with low vitamin E levels had lower antioxidative activity, making them less protective against diseases and herbivores [70].

As a result, $^1O_2$ in chloroplasts is physically destroyed by tocopherols. One molecule of α-tocopherol can disable up to 120 molecules of $^1O_2$ prior to breakdown by resonance energy transfer[71]. Tocopherols are also potential candidates for modulating cellular signaling in plants since they are part of a complex signaling network controlled by ROS, antioxidants, and phytohormones [71]. Environmental variables and stress-sensitive phytohormones, including salicylic acid, abscisic acid, and jasmonic acid, have an impact on tocopherol synthesis [66]. α-tocopherol alterations occur in two stages during plant's response to environmental stress. Under stress, α-tocopherol concentration rises and has a preventive effect via reducing ROS levels in the first step.

When stress is too great in the second phase, α-tocopherol degradation exceeds synthesis. The first phase occurs only in stress-tolerant plants, whereas the second stage is common in stress-sensitive plants. Tocopherol content in photosynthetic species has changed in response to adverse environmental circumstances such as dryness, heavy metals, salt, or bright light [72].

5-Carotenoids (Car)

Carotenoids are another important class of herbal compounds that can be used as nutraceuticals or simply as part of a healthy diet to help with a variety of diseases. Carotenoids are of different types tetraterpene. Isoprenoid units, which are produced by either head-to-tail or tail-to-tail biosynthesis, make up the carotenoid structural backbone. Isoprenoids, or carotenoids, have a C40 moral backbone and a fundamental structure made up of eight isoprene units. Carotenes and xanthophylls are the two kinds into which they fall [73].

Xanthophylls are derivatives that contain oxygen, whereas carotenes are pure hydrocarbons. In chloroplasts, carotenoids have two crucial roles: they capture light energy for use in photosynthesis and are critical components of the antioxidant defense mechanism that guards against photodamage to the photosynthetic system [74]. In low light conditions, carotenoids may function as active antennas that transport energy to chlorophylls or bacteriochlorophylls

at photochemical reactions by absorbing sun radiation at wavelengths that chlorophylls could not absorb (RCs).

They increase the range of light available for photosynthesis in this way. Additionally, carotenoids serve as the structural foundation for the higher plant LHCs, LH1, LH2, and other sunlight complexes that are external to reaction site [75].

Carotenoids, on the other hand, have been demonstrated to function as photoprotectors in photosynthetic units, preventing photosystem self-oxidation, by acting as chelating agents of potentially dangerous chlorophyll (or bacteriochlorophyll) triplet states and singlet molecular oxygen (PSO) [76]. Babaei et al. [77] discovered that -carotene effectively reduced salt stress. Furthermore, β-carotene increased creeping bentgrass heat tolerance by increasing the metabolism of enzymatic antioxidants, notably those in the AsA-GSH and water-water cycles, offering protection when antioxidant enzyme activity was substantially decreased by heat stress [78].

Conclusions:

Plants react to various stressors by modifying their physiological and biochemical characteristics, including growth, protein breakdown, lipid peroxidation, and DNA damage, which results in free radicals and other ROS that cause cellular harm. To minimize the harmful effects of oxygen species, plants excrete specific metabolites such as soluble proteins and antioxidants. Plant cells were widely examined in terms of an antioxidant defense mechanism, such as nonenzymatic and enzymatic compounds, to overcome crop production limits. Stress resistance is thought to be dominated by AsA, reduced glutathione, flavonoids, vitamin E, and carotenoids, with each contributing significantly to their antioxidant capacity.

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مضادات الأكسدة غير الأنزيمية في النباتات المجهدة: مراجعة

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الخلاصة:

تتعرض النباتات لمختلف الاجهادات البيئية خلال دورة حياتها وتتكون نتيجة لهذه الضغوط الجذور الحرة. جذور الاوكسجين الحرة لها دور مهم في الحفاظ على نمو النبات بصورة طبيعية وزيادة تحمله للإجهادات . اختلال التوازن بين تكوين الجذور الحرة ومضادات الاكسدة الدفاعية من اهم أثار الاجهادات الحيوية وغير الحيوية مما يؤدي الى زيادة تراكم الجذور الحرة والاجهاد التأكسدي في النباتات. تميل النباتات إلى مواجهة هذه المشكلة من خلال قدرتها على تصنيع المواد المعادلة للجذور الحرة للاوكسجين، وتحافظ أنظمة الدفاع المضادة للأكسدة الأنزيمية وغير الأنزيمية على التوازن بين إزالة السموم وإنتاج أنواع الأكسجين التفاعلية. في هذا السياق ، يعد حمض الأسكوربيك (AsA) والكلوتاثايون (GSH) والفلافونويد وفيتامين E والكاروتينات من مضادات الأكسدة غير الأنزيمية المهمة التي لها قدرة كبيرة ليس فقط في اقتناص الجذور الحرة للاوكسجين ولكن أيضًا العديد من الوظائف الأساسية في النباتات تحت ظروف الإجهاد وغير المجهدة. توضح هذه المراجعة أهم الأدوار الرئيسية لبعض مضادات الأكسدة غير الأنزيمية في النباتات التي تتعرض لأنواع مختلفة من الاجهادات الحيوية وغير الحيوية.

الكلمات المفتاحية : حامض الاسكوربيك، الكلوتاثايون ، فيتامين E ،الكاروتينات ،الفلافونويدات