Oxalic acid/oxalates in plants: from self-defence to phytoremediation

Rajendra Prasad and Yashbir Singh Shivay*

Division of Agronomy, ICAR-Indian Agricultural Research Institute, New Delhi 110 012, India

Oxalic acid and oxalates are produced and present in plants in different amounts. Insoluble calcium oxalate plays a key role in regulating calcium concentration, which is important in the functioning of guard cells. Oxalates provide tolerance to aluminium toxicity to plants growing in acid soils. Both oxalic acid and calcium oxalate provide self-defence against insect pests and grazing animals. Oxalates are involved in phytoremediation of soils rendered toxic by heavy metals, like lead, cadmium, zinc, etc.

Keywords: Aluminium toxicity, calcium oxalate, oxalic acid, phytoremediation.

OXALIC acid and oxalates are present in leaves, roots, stems, fruits and seeds of many plants. Oxalic acid is a dicarboxylic acid with the formula [HOOC.COOH] or $H_2C_2O_4$. Its acidic strength is greater [pKa = 1.27 for the dissociation of the first H^+] than that of acetic acid [pKa = 4.76]; it is probably the strongest organic acid in plants. It is a reducing agent and its conjugate base $[C_2O_4]^{-2}$ is a chelating agent for cations such as Ca, Mg, Zn, Mn, Fe, etc.[1]. Oxalic acid reacts with cations resulting in the formation of different oxalates. The solubility in water (20°C/25°C) of oxalic acid is 143 g l^{-1}, while that of sodium, potassium and magnesium oxalates is 37.0, 39.3 and 1.2 g l^{-1} respectively. In contrast, the solubility of calcium oxalates is only 0.67 mg l^{-1}. Because of its metallic ion-chelating properties, oxalic acid is widely used for bleaching purposes in dying industry, especially for removing rust spots. It is also used for the restoration of old wood.

Production of oxalic acid in plants

Oxalic acid was isolated from the extract of a rhizomatous plant wood sorrel (*Oxalis acetosella*) as early as 1773 by Francois Pierre Savary in Switzerland[2]. Oxalates may constitute as much as 3–10% of plant dry mass[3]. Three pathways for oxalate biosynthesis in plants have been suggested, namely oxidation of glycolate/glyoxylate during photorespiration[3], oxaloacetate breakdown presumably catalysed by an oxaloacetase[4,5] and from ascorbic acid breakdown[3,6]. However, the relative contribution of these pathways is controversial. For example, Xu *et al.*[7] observed that oxalate accumulation and regulation are independent of glycolate oxidation in rice, while Yu *et al.*[8] observed that glyoxylate rather than ascorbate are an efficient precursor for oxalate biosynthesis.

Functions in physiological processes

It is suggested that oxalate synthesis is related to the regulation of the balance between inorganic cations (K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}) and anions (NO_3^-, Cl^-, $H_2PO_4^-$, SO_4^{-2}) in plant cells[9]. Formation of insoluble calcium oxalate enables plants to regulate the concentration of calcium and oxalic acid, both of which can be toxic when in excess[10]. For example, Ca is well known to play an important role in signal transduction in stomatal guard cells, but a higher than desired concentration of Ca inhibits this function. Regulation of Ca by calcium oxalate was shown by Ruiz and Mansfield[11] in the case of *Cummlina communis* L. Insoluble calcium oxalate formation is suggested as a mechanism of storing Ca for future needs of the plant[12,13].

Protection from insect pests and grazing animals

Oxalic acid and oxalates provide biochemical as well as mechanical defence against insect pests and animals[3,14,15]. Leaves of non-edible plants of *Arisaema* sp. (known as cobra lily) found in China and Japan, contain very high levels of calcium oxalate and are toxic. Soluble oxalates are reported to be toxic to plant hoppers[16] and other insects. High oxalate-containing grasses are reported to be toxic to grazing cattle[17,18]. For ruminants, Sidhu *et al.*[19] reported a critical limit of 3.01% oxalate in Napier grass (*Pennisetum purpurea*). Death of a large number of sheep due to oxalate toxicity by grazing on poisonous weed *Halogeton glomeratus* has been reported[20]. Calcium oxalate is fairly toxic and even a small dose is enough to cause sensation of burning in the mouth, and swelling and choking of throat. With regards to insoluble oxalate, some plants such as *Tragia ramosa*[21] and *Medicago tranculata*[22] produce needle-shaped hairs, which can puncture the dermis of insects and thus keep them away.

*For correspondence. (e-mail: ysshivay@hotmail.com)

Presence of calcium oxalate minerals (also referred to as biominerals) whewellite and weddellite has been reported in several species of cacti (*Opuntia* species)[23,24]. Weddellite druses are made up of tetragonal crystallites, whereas those of whewellite have acute points and general star-like shape. Keeping this in view, Nakata[25] has suggested genetically engineered formation of calcium oxalate in plants to reduce insect damage.

As a chemical secreted by fungi to infect plants

Fungi such as *Sclerotium rolfsii* Sacc[26] and *Sclerotinia sclerotiorum*[27] secrete oxalic acid to infect the plants. Oxalic acid acts as a signalling molecule to induce a genetically regulated apoptotic-like programmed cell death (PCD) in host plant tissue[28]. Thus, the fungus tricks the host into generating nutrient-rich dead cells that are of sole and direct benefit to it[29].

Overcoming aluminium toxicity

Acid soils account for approximately 40% of the arable land on earth. Exchangeable aluminium (Al^{3+}) in soil solution has been identified as a major cause for soil acidity[30] and its toxicity is the limiting factor for crop productivity on such soils[31,32]. Some crops such as cotton (*Gossypium* sp.), sorghum (*Sorghum bicolor*) and alfalfa (*Medicago sativa*) are sensitive to Al toxicity and need liming to nearly zero level of Al-saturation for successful crop growth[33]. Morita *et al.*[34,35] demonstrated that oxalate was a key compound in the Al-tolerance mechanism employed by the tea plant, which detoxifies Al^{3+} externally in the rhizosphere. Similarly, oxalic acid is secreted from the roots of buckwheat (*Fagopyrum esculentum* Moench, cv. Jianxi)[36,37], which also shows high Al-tolerance.

Role in phytoremediation

Oxalic acid is also reported to help in the accumulation of heavy metals, cadmium, nickel, zinc, etc. by hyper-accumulators[38–41], which are being utilized in phytoremediation of soils affected by toxicity of these heavy metals. This toxicity in soils may be caused by the continuous use of sewage sludge[42] or closeness to zinc or lead smelters[43–45] or due to other natural causes. About 400 species of 45 plant families, including Brassicaceae, Fabaceae, Euphorbeaceae, Asteraceae, Laminaceae and Scorphubariacea have been identified as hyper-accumulators of heavy metals[46]. A study in Macedonia recommended alfalfa for the phytoremediation of soils made toxic with lead, oilseed rape (*Brassica napus*) and white clover (*Trifolium repens* L.) for toxicity with cadmium, and alfalfa and white clover for toxicity with zinc[45]. Of special interest is arsenic toxicity of groundwater in eastern India and Bangladesh[47,48] and several other countries of the world[49]. Large intake of arsenic results in lung, kidney and bladder cancer and several other ailments[50]. Recently, Chintakovid *et al.*[51] from Thailand reported that Nugget marigold, a tetraploid hybrid between American *Tagetes erecta* L. and French *T. patula* L, could be a good phytoremediater for arsenic; arsenic content was 46.2% in the leaves and 5.8% in the flowers.

Conclusion

Oxalic acid and oxalates play an important role in maintaining the desired Ca concentration in cells, self-defence against insect pests and grazing animals and thus phytoremediation, and thus deserve further attention.

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ACKNOWLEDGEMENTS. We thank the Director, Joint Director (Research) and Head, Division of Agronomy, ICAR-Indian Agricultural Research Institute, New Delhi for their advice and support.

Received 26 September 2016; revised accepted 7 February 2017

doi: 10.18520/cs/v112/i08/1665-1667