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Current knowledge and future research perspectives on cassava (*Manihot esculenta* Crantz) chemical defenses: An agroecological view

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A B S T R A C T

Cassava (*Manihot esculenta* Crantz) is one of the most important staple crops worldwide. It constitutes the major source of carbohydrates for millions of low-income people living in rural areas, as well as a cash crop for smallholders in tropical and sub-tropical regions. The Food and Agriculture Organization of the United Nations predicts that cassava plantations will increase and production systems will intensify in the future, highlighting the need for developing strategies that improve the sustainability of production. Plant chemical defenses hold the potential for developing pest management strategies, as these plant traits can influence the behavior and performance of both pests and beneficial arthropods. Cassava plants are well-defended and produce a number of compounds involved in direct defense, such as cyanogenic glycosides, flavonoid glycosides, and hydroxycoumarins. In addition, volatile organic compounds induced upon herbivory and the secretion of extrafloral nectar act as indirect defense against herbivores by recruiting natural enemies. Here, cassava chemical defenses against pest arthropods are reviewed, with the aim of identifying gaps in our knowledge and areas of research that deserve further investigation for developing sound pest control strategies to improve sustainable production of this crop, and how these defenses can be used to benefit other crops. Cyanogenic content in cassava is also highly toxic to humans, and can cause irreversible health problems even at sub-lethal doses when consumed over prolonged periods. Therefore, the promotion of chemical defense in this crop should not aggravate these problems, and must be accompanied with the education on processing methods that reduce human exposure to cyanide.

1. Introduction

Cassava (*Manihot esculenta* Crantz) is a perennial shrub belonging to the Euphorbiaceae family. From a socio-economic point of view, it is one of the most important crops in tropical and sub-tropical regions worldwide. In its native range of South America, where it was domesticated many thousands of years ago (FAO, 2013; McKey et al., 2010), and in Africa, where it was introduced during the 16th century, cassava is one of the most important staple food sources for low-income families in rural areas and a primary cash crop for smallholders. In contrast in Asia, cassava was introduced much later, about two hundred years ago (Howeler, 2000), and is mainly grown for exporting industrialized products (dried chips, pellets and starch for animal feed and industry) as well as for fuel production (FAO, 2013; Zhou and Thomson, 2009). In terms of food security, the importance of this crop relies on several plant traits. Cassava accumulates starch in the root parenchyma, making this starchy organ an important source of carbohydrates. Roots also contain significant levels of vitamin C, riboflavin, thiamin and niacin (FAO, 1997). Currently this crop feeds more than 800 million people worldwide (FAO, 2013). Moreover, plants are adapted to grow fairly well in marginal soils and withstand severe conditions of heat and drought, which makes cassava a key crop in arid regions, as well as under the predicted changes in climatic conditions (Burns et al., 2010; Rosenthal et al., 2012). Smallholders seldom spray pesticides in cassava plantations, as chemical control is not economically viable. However, since plantations of cassava are expected to expand in the future (FAO, 2013), this situation may

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change, due to the pressures to intensify production under modern agricultural paradigms.

For increasing sustainability of production systems, pest control strategies that are environmentally friendly and economically accessible to growers need to be developed and implemented. Plants are active components of multitrophic interactions and in order to develop sound pest management strategies, it is essential to understand the ecology of diversified agroecosystems (Lewis et al., 1997) and exploit the plant's own defenses. Chemical defenses against herbivores in plants include an array of volatile and non-volatile compounds that can negatively affect behavior and performance of arthropod herbivores (direct defenses) or enhance the activity of natural enemies that exert biological control (indirect defenses) (Mithöfer and Boland, 2012). These defenses can be expressed constitutively, without requiring any abiotic or biotic stress for synthesis. In addition to constitutive expression, chemical defenses can be induced upon herbivore damage or other types of environmental stress (Chen, 2008; Karban and Baldwin, 1997; Turlings and Wäckers, 2004).

Cassava plants are well-defended and possess an array of chemical strategies involved in both bottom-up (resource-based) and top-down (enemy-based) herbivore regulation. It has been argued that chemical defenses of cassava underlie the agronomical advantages of this crop (McKey et al., 2010 and references therein). Perhaps, because of the occurrence of these defense mechanisms, there is a number of herbivores associated with this plant (Table 1) but only a few species have the potential to cause yield losses (Bellotti et al., 1999; FAO, 2013). Cyanogenic glycosides comprise the most studied group of chemical defenses, probably because of the well-known toxicity of these compounds to arthropods and other animals. Cyanide produced from the breakdown of the glycoside is an effective poison even for plants. Due to the cyanogenic potential of this species, consumption of insufficiently processed cassava poses risks to human health. Acute intoxication with cyanide can cause vomiting, tachypnea, tachycardia dizziness, headache, abdominal pain, diarrhea, mental confusion and convulsions (Cliff et al., 1997). In addition, prolonged exposure to cyanide at sub-lethal doses, such as continued consumption of insufficiently or incorrectly processed cassava, can cause irreversible neurological diseases, such as Konzo and tropical ataxic neuropathy (TAN), among other serious disorders (Nhassico et al., 2008). In addition to cyanogenic glycosides, however, cassava leaves and/or roots contain other compounds such as different phenolics and terpenoids (Blagbrough et al., 2010; Montagnac et al., 2009). Moreover, cassava plants emit volatile organic compounds (VOCs) and secrete extrafloral nectar (EFN), all of which play an important role in biological control. Burns et al. (2010) suggest that boosting natural chemical defenses of cassava plants can improve sustainability of production of this crop. Here, the current state of knowledge on the chemistry of cassava plants is reviewed from the perspective of the ecology of plant-insect interactions focusing on plant defenses against arthropod herbivores. Therefore, the aim is to identify knowledge gaps and areas of research that deserve further attention in the exploitation of chemical defenses of cassava in the light of sustainable agricultural production.

2. Direct defenses

2.1. Cyanogenic glycosides

Cyanogenic glycosides are relatively widespread in the plant kingdom and constitute an important group of secondary metabolites involved in plant defense against arthropod herbivores (Gleadow and Møller, 2014). Chemically, they are composed of an α-hydroxynitrile type aglycone and a sugar moiety (mostly D-glucose) (Vetter, 2000). In cassava, L-valine-derived linamarin (**1**) and L-isoleucine-derived lotaustralin (methyl linamarin) (**2**) (Fig. 1) are the most abundant cyanogenic glycosides and account for, respectively, over 90% and under 10% of total cyanogenic compounds in cassava (McMahon et al., 1995). There is, however, considerable genetic variation in the levels of cyanogenic glycosides (Burns et al., 2012). In addition, environmental factors such as nitrogen supply (Jørgensen et al., 2005) and water deficit (Cardoso et al., 1999) contribute significantly to the cyanogenic content of plants. The biosynthesis of these compounds occurs commonly in shoots from where they translocate to roots (Jørgensen et al., 2005), though low quantities of cyanogenic glycosides are also biosynthesized in the roots (McMahon et al., 1995). Therefore, cyanogenic glycosides are present in all plant tissues but mainly in the leaves (Jørgensen et al., 2005; White et al., 1998). The enzyme linamarase is synthesized in the laticifers (Pancoro and Hughes, 1992) and is concentrated in the latex where its activity has been reported to be more than 300-fold higher than in leaves (Nambisan, 1999). Cyanogenesis in cassava starts when the vacuole releases linamarin (**1**) and lotaustralin (**2**) upon cell rupture, which commonly occurs during mechanical damage or feeding by chewing herbivores, and these compounds encounter the hydrolyzing enzymes. Degradation of cyanogenic glycosides by linamarase results in the formation of an unstable cyanohydrin (**10**). This compound can be broken down enzymatically by α-hydroxynitrile lyase (HNL), or be spontaneously decomposed at pH greater than 5.0 or temperatures over 35 °C (Fig. 2) (White et al., 1998) to form acetone and hydrogen cyanide (HCN), both being highly toxic to herbivores (Mithöfer and Boland, 2012).

The role of linamarin (**1**), lotaustralin (**2**) and the linamarin-deglycosylated form acetone cyanohydrin in plant defense has been studied in several combinations of herbivores and plants (for a review, see Gleadow and Woodrow, 2002; Nahrstedt, 1985). As a general rule, strongly cyanogenic plants are protected from generalist rather than specialist herbivores (Ballhorn et al., 2010; for a review, see Gleadow and Woodrow, 2002). Cyanogen content in cassava leaves is known to deter the generalist grasshopper *Zonocerus variegatus* (Orthoptera: Pyrgomorphidae) from feeding (Bellotti and Riis, 1994; Bernays et al., 1977). This species prefers to feed on senescent or wilting leaves (Bernays et al., 1977) that release HCN more slowly compared to younger growing leaves. Only starved adult grasshoppers can feed on growing cassava leaves, but they progressively lose weight, whereas nymphs do not accept growing leaves at all (Bernays et al., 1977). Negative effects of cyanogenic glycosides are also reported for the generalist burrowing bug *Cyrtomenus bergi* (Hemiptera: Cydnidae), a root feeder in cassava plantations. Intracellular penetration of the stylet in the root parenchyma during feeding results in the accumulation of linamarin (**1**) in the hemolymph causing greater nymphal mortality, particularly during early instars. Adults fed on clones with high cyanogenic levels showed lower longevity and fecundity but not significantly higher death rates (Bellotti and Riis, 1994; Riis et al., 2003). The longer stylet of adults allows them to feed beyond the outer layers or cortex of the roots, where the larger linamarin (**1**) contents occur, which results in better performance of adults compared to nymphs (Bellotti and Arias, 1993). A study on the preference of whiteflies *Bemisia tabaci* (Hemiptera: Aleyrodidae) for cassava varieties with different levels of "bitterness" found fewer insects settled on the most "bitter" varieties (Dengel, 1981) suggesting that preference is negatively affected by higher cyanogenic glycoside contents. Beyond these few examples, we are not aware of other studies assessing the effect of cyanogenic glycosides on other herbivores associated with cassava. However, cyanogenic glycosides may also be involved in the resistance against other generalist herbivores attacking this crop. From studies in *Lotus*

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