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Cyanogenic Interaction Between Arthropods and Plants

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Abstract

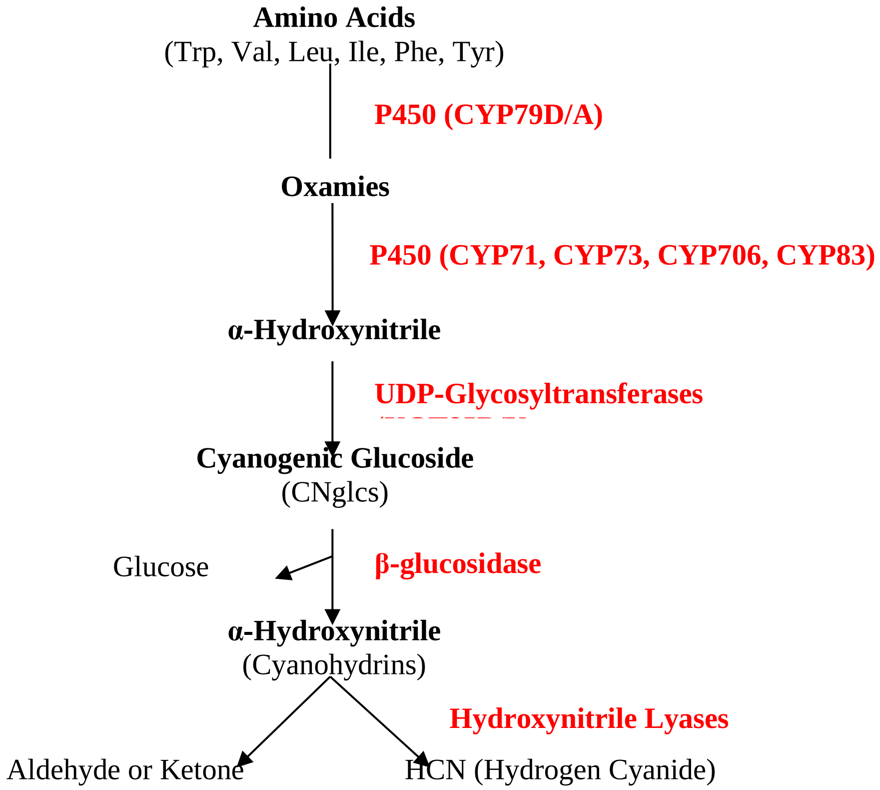
Cyanogenesis is a vital chemical defense mechanism employed by both plants and certain arthropods. This process involves the synthesis, storage, and release of hydrogen cyanide (HCN) as a deterrent against herbivores and predators. Cyanogenic glucosides (CNGs), derivatives of amino acids, are key intermediates in cyanogenesis. While over 2,500 plant species are known to contain cyanogenic compounds, this ability is comparatively rare among animals, being primarily observed in arthropods. Arthropods, such as insects, millipedes, centipedes, and mites, have evolved mechanisms to either sequester or biosynthesize cyanogenic compounds from their host plants. These compounds not only protect them against predators but also play a crucial role in their ecological interactions. In particular, cyanogenic compounds like cardiospermin, linamarin, and mandelonitrile are prominent in these defense strategies. Understanding the biosynthesis and functional role of cyanogenic compounds reveals the intricate chemical warfare between plants, arthropods, and their predators.

Keywords: Cyanogenesis, Cyanogenic glucosides (CNGs), Arthropods, Chemical defense

Introduction:

Cyanogenesis in arthropods refers to the ability of certain arthropods to produce and release hydrogen cyanide (HCN) as a defense mechanism against predators or it also refers to a chemical defense mechanism in which hydrogen cyanide (HCN, also known as hydrocyanic or prussic acid) is generated, stored, and released in response to an attack (Brueckner *et al*., 2017) and the process accelerates under alkaline conditions and temperatures above 60°C (Park and Coats 2002). Cyanogenic glucosides (CNGs) are β-glycosides of α-hydroxynitriles, also known as cyanohydrins. They are derived from aliphatic protein amino acids such as L-valine, L-isoleucine, and L-leucine, aromatic amino acids like L-phenylalanine and L-tyrosine, and the aliphatic non-protein amino acid cyclopentenyl-glycine (Bak *et al*., 1998). Cyanogenic glucosides (CNglcs) are found in over 2,500 plant species, but in animals, they seem to be limited to arthropods (Duffey, 1981). In plants, Cyanogenic glucosides (CNglcs) are stored in the vacuoles (Vetter, 2000) and play a key role in plant defense against herbivores due to their bitter flavour and the release of toxic hydrogen cyanide (HCN), along with ketones or aldehydes, when plant tissue is damaged. Linamarin and lotaustralin, two common aliphatic CNglcs, are the most prevalent in both plants and insects and are typically found together (Lechtenberg and Nahrstedt, 1999). Additionally, CNGs are known to function as both feeding deterrents and phagostimulants for herbivores depending on the herbivore species feeding on the plants containing CNglcs (Gleadow and Woodrow, 2002). Major food crops that contain cyanogenic glucosides (CNGs) include cassava (*Manihot esculenta*), sorghum (*Sorghum bicolor*), giant taro (*Alocasia macrorrhizos*), bamboo (*Bambusa vulgaris*), apple (*Malus domestica*), and apricot (*Prunus armeniaca*) (Nyirenda, 2020). This cyanogenesis process is most commonly observed in some species of insects (Heteropterans, Coleopterans and Lepidopterans), millipedes (Diplopods), centipedes (Chilopods) and mites (Arachinids) (Dar *et al*., 2016). Certain specialized herbivores, particularly insects, selectively feed on cyanogenic plants. These herbivores have developed the ability to either metabolize cyanogenic glucosides or sequester them for their own defense against predators (Zagrobelny and Moller (2011).

Steps in biosynthesis of Cynogenic compounds



Step 1. Amino Acid to Oxime: The process starts with an amino acid, which is converted into an oxime. This transformation is catalyzed by an enzyme referred to as P450.

Step 2. Oxime to α-Hydroxynitrile: The oxime is then converted into a compound called α-hydroxynitrile (also known as cyanohydrin). This reaction is facilitated by another enzyme, P450.

Step 3. Formation of Cyanogenic Monoglucoside: The α-hydroxynitrile is then glycosylated, means a sugar molecule (glucose) is added to it. This step is catalyzed by an enzyme known as UDP-glucosyltransferase, using UDP-glucose as a sugar donor. The result of this process is the formation of a cyanogenic monoglucoside.

Step 4. Structure of Cyanogenic Monoglucoside: The structure of the cyanogenic monoglucoside is shown in the image, where R1 and R2 represent variable side chains attached to the molecule. The key feature of this structure is the presence of the cyanide group (-C≡N), which can be released under certain conditions.

This pathway is crucial in plants for producing defense compounds that can release cyanide when the plant is damaged, deterring herbivores and pathogens (Boter and Diaz 2023).

Table 1: Cynogenic compounds in different crops

S.No	Cynogenic compound	Plants	Plant parts	Reference
1.	Amygdalin, Prunasin	Bitter almond	Kernels	Nyirenda, 2020
2.	Amygdalin, Prunasin	Apricot	Kernels	
3.	Amygdalin	Apple	Seeds	
4.	Amygdalin, Prunasin	Peach	Kernels	
5.	Amygdalin, Prunasin	Nectarine	Kernels	
6.	Taxiphyllin	Bamboo	Shoots	
7.	Taxiphyllin	Giant taro	Leaves	
8.	Dhurrin	Sorghum	Young leaves	
9.	Linustatin	Flax	Seeds	
10.	Linmarin	Lima beans	Seeds	
11.	Lotaustralin	Cassava	Roots	
12.	Dhurrin	Cocoyam	Leaves and roots	

Table 2: Cynogenic compounds in different insect orders

S.No	Cynogenic compound	Species	Reference
1.	Benzaldehyde, benzoic acid, benzoyl cyanide, mandelonitrile, mandelonitrile benzoate	*Niponia nodulosa*	Kuwahara *et al*., 2015
2.	Benzaldehyde, HCN	*Euryurus maculates, Euryurus leachii*	Duffey *et al*., 1977
3.	p-isopropyl mandelonitrile glucoside	*Polydesmus vicinus*	Duffey *et al*., 1981
4.	Mandelonitrile benzoate	*Polydesmus collaris*	Tower *et al*., 1972
5.	HCN	*Pseudopolydesmus canadensis*	Eisner *et al*., 1978

6.	Benzaldehyde, HCN mandelonitrile hexanoate	*Orbitula tibialis*	Brueckner *et al*., 2017
7.	Cynamide	*Aphis craccivora*	Kamo *et al*., 2012
8.	Cyanolipids, HCN	*Jadera sanguinolenta*	Aldrich *et al*., 1990
9.	Cardiospermin	*Leptocoris isolata*	Braekman *et al*., 1982
10.	Cycasin	*Seirarctia echo*	Duffey *et al*., 1981
11.	Sarmentosin	*Yponomeuta hexabolus*	Nishida, 2002

Chemical defence in arthropods:

The secretion from *Himantarium gabrielis* included HCN, benzaldehyde, benzoyl cyanide, benzyl cyanide, mandelonitrile and mandelonitrile benzoate, among other components. Similarly, the secretion from *Geophilus vittatus* contained benzaldehyde, benzoic acid, benzoyl cyanide, HCN, and mandelonitrile, with a pH ranging from 6 to 6.5. These substances were also utilized by females for egg protection.

Leptocorisa isolata larvae have the cyanogenic compound cardiospermin in their haemolymph, which is likely derived from cyanolipids obtained from their host plant. Cardiospermin was found to repel ants. However, adult insects did not possess this compound, possibly indicating that costly defensive chemicals are conserved for life stages that are more susceptible to predation.

Beetles release defensive secretions from vesicles located on their hind body, and exposure to the defensive secretion of *Paropsis atomaria* resulted in the death of ants within 2 minutes.

Conclusion:

Cyanogenic interactions between arthropods and plants underscore the sophisticated chemical defenses employed in nature. Arthropods that sequester or synthesize cyanogenic compounds demonstrate a highly effective strategy for deterring predators. The presence of hydrogen cyanide and related cyanogenic compounds in both plants and arthropods highlights a co-evolutionary relationship, where specialized herbivores adapt to toxic defenses for their own survival and protection. This interplay reflects not only the adaptive capabilities of arthropods but also their dependency on plant-derived chemicals. The biosynthesis of cyanogenic compounds, particularly in vulnerable life stages, shows the allocation of resources towards crucial survival strategies. Consequently, cyanogenesis remains a critical aspect of plant-insect interactions, influencing ecological dynamics and contributing to the survival of numerous species across ecosystems.

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