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A Review of Cyanogenic Glycosides in Edible Plants

Islamiyat Folashade Bolarinwa,
Moruf Olanrewaju Oke,
Sulaiman Adebisi Olaniyan and
Adeladun Stephen Ajala

Additional information is available at the end of the chapter

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Abstract

Cyanogenic glycosides are natural plant toxins that are present in several plants, most of which are consumed by humans. Cyanide is formed following the hydrolysis of cyanogenic glycosides that occur during crushing of the edible plant material either during consumption or during processing of the food crop. Exposure to cyanide from unintentional or intentional consumption of cyanogenic glycosides may lead to acute intoxications, characterized by growth retardation and neurological symptoms resulting from tissue damage in the central nervous system (CNS). Processing methods can detoxify cyanogenic glycosides and reduce the risk of cyanide poisoning. The efficiency of cyanide removal, however, depends on the processing technique employed and the extent of processing. Processing operations such as fermentation, boiling/cooking, and drying, applied to process food-containing cyanogenic glycosides have been reported to reduce cyanide content to acceptably safe levels. The present review discusses the level of cyanogenic glycosides in specific plant foods, health implications of consuming cyanogenic plants and effect of various processing method on cyanogenic glycosides with updated information gathered from the published reports on cyanogenic glycosides.

Keywords: cyanogenic glycosides, cyanide, toxins, processing, cyanide poisoning, food safety

1. Introduction

Food plants contain many substances that can pose potential risks to consumers, and one of these types of substances is cyanogenic glycosides. Cyanogenic glycosides are chemical compounds contained in foods that release hydrogen cyanide when chewed or digested. The act of chewing or digestion leads to hydrolysis of the substances, causing cyanide to be released [1]. Cyanogenic glycosides are common in certain families such as the Fabaceae, Rosaceae, Leguminosae, Linaceae, and Compositae, and identification of their constituents is a useful tool for informative taxonomic markers [2]. There are approximately 25 known cyanogenic glycosides and these are generally found in the edible parts of plants, such as apples, apricots, cherries, peaches, plums, quinces, particularly in the seed of such fruits. The chemicals are also found in almonds, stone fruit, pome fruit, cassava, bamboo shoots, linseed/flaxseed, lima beans, coco yam, chick peas, cashews, and kirsch [3, 4]. Other food products that may contain cyanogenic glycosides include some food ingredients with flavoring properties such as ground almonds powder or paste, marzipan, stone fruit, and alcoholic drinks made from stone fruits. These foods therefore represent potential sources of hydrogen cyanide [5].

The toxicity of cyanogenic glycosides and their derivatives is dependent on the release of hydrogen cyanide. Toxicity may result in acute cyanide poisoning and has also been implicated in the etiology of several chronic diseases [6, 7]. Cyanide toxicity can occur in animal including humans at doses between 0.5 and 3.5 mg HCN per kilogram body weight. Symptoms of cyanide toxicity in humans have been reported to include vomiting, stomach ache, diarrhea, convulsion, and in severe cases death [5]. Children are particularly at risk because of their smaller body size [1].

The toxicity of cyanogenic glycosides is associated with their ability to be hydrolyzed either spontaneously or in the presence of enzyme to produce cyanide as end products of their hydrolysis. Thus, toxic levels of cyanogenic glycosides are estimated in terms of the quantity of free cyanide generated following hydrolysis. This makes it difficult to estimate total cyanogenic glycosides in diet. Hence, levels of amygdalin (the most common cyanogenic glycosides in fruits) reported in literature are inconsistent [8]. Although the level of cyanide up to 10ppm was reported by World Health Organization (WHO) to be safe for cassava flour [9]. Lack of quantitative toxicological test and epidemiological information makes it difficult to establish safe level of cyanogenic glycosides intake in many foods.

Cyanogenic glycosides are a group of nitrile-containing plant secondary compounds that yields cyanide (cyanogenesis) following their enzymatic breakdown. Cyanogenic glycosides occur in at least 2000 plant species, of which a number of species are used as food. They are amino-acid-derived constituents of plants produced as secondary metabolites [5]. Despite great deal of structural diversity in cyanogenic glycosides, almost all of them are believed to be derived from only six different amino acids L-valine, L-isoleucine, L-leucine, L-phenylalanine, or L-tyrosine, and cyclopentenyl-glycine (a nonprotein amino acid) [2, 10]. Cyanogenic glycosides play pivotal roles in organization of chemical defence system in plants and in plant-insect interactions [10].

Cyanogenic glycoside is not toxic on its own. However, when cell structures of plant are disrupted, cyanogenic glycoside will be brought together with the corresponding β -glucosidase enzyme. Hydrolysis of cyanogenic glycosides usually occurs when cyanogenic plants are chewed by herbivores or when the plants are disintegrated during processes, such as grinding, pounding or in the presence of water for example during soaking or fermentation [11]. Hydrolysis is accomplished by the β -glucosidase, producing sugars and a cyanohydrin that spontaneously decomposes to HCN and a ketone or aldehyde [11, 12]. Different kinds of cyanogenic glycosides may be found in different cyanogenic food plants, for example, taxiphyllin in bamboo shoots, linamarin in cassava [5]. Several commercial crop plants, such as sorghum (*Sorghum bicolor*), apple, apricot, almond kernels cassava (*Manihot esculenta*), and barley (*Hordeum vulgare*), are cyanogenic and accumulate significant amounts of cyanogenic glycosides [2, 13, 14]. Generally, the level of cyanogenic glycosides produced is dependent upon the age and the variety of the plant, as well as environmental factors [2].

2. Cyanogenic plant foods

2.1. Cassava

High levels of cyanogenic glycosides have been reported to be present in many nutritious dense plants, thus limiting the use of some of the plants as food. For instance, cassava (*Manihot esculenta*) is one of such plant with high amount of cyanogenic glycosides. It is a crop of economic importance in Africa and a staple food in most African communities [15]. Cassava is also a valued crop in South America and Southeast Asia. The high carbohydrate content of the crop makes it a good source of calorie for feeding billions of people in the world [16]. According to Food and Agriculture organization, cassava is the third most important source of calories in the tropics, after rice and corn [1, 9]. Cassava leaves have higher protein content, contain vitamin C and vitamin A and provide some dietary fiber [17]. Much of the protein in the leaves is made up of linamarase, the enzyme that detoxifies the cyanogenic glycosides in cassava [18]. However, each parts of cassava plants (leaves, stem, root) contains high levels of cyanogenic glycosides; linamarin, lotaustralin, and amygdalin [14, 19], with linamarin been the most predominant cyanogen [19].

The cyanide level of cassava varies from about 75 to 350 ppm, but can be up to 1000 ppm or more depending on the variety, plant age, soil condition, fertilizer application, weather, and other factors [20]. Studies have shown that the levels of cyanogenic glycosides in cassava roots are generally lower than that in the leaves and stems [21, 22]. Cassava roots have been reported to contain cyanide content of 10–500 mg/kg of dry matter [23] and the leaves were reported to contain 53–1300 cyanide equivalents/kg of dry matter [24].

Cassava root is processed into various forms before consumption. The root can be boiled and eaten as whole root, or processed into flour for the production of “thick gruel” commonly consumed in Africa. It can also be converted into chips for the production of flour, tapioca, and other foods. Cassava leaves are used in some African countries to produce soup or sauce, following processes such as scrubbing, fermentation, pounding, and boiling. Apart from

human consumption, cassava roots and peels are also consumed by animal [1]. The major cyanogenic glycoside in cassava is linamarin, while small amount of lotaustralin (methyl linamarin) and amygdalin are also present, as well as an enzyme linamarase. Linamarin is rapidly hydrolyzed by linamarase to glucose, acetone cyanohydrin, and hydrogen cyanide (Figure 1).

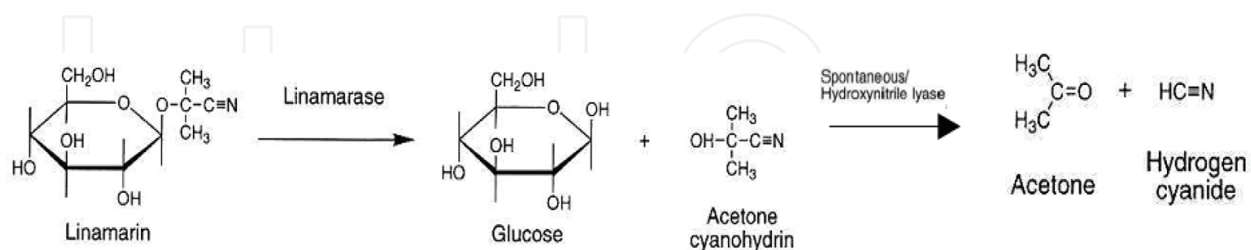


Figure 1. Hydrolysis of linamarin to produce hydrogen cyanide.

Under neutral conditions, acetone cyanohydrin decomposes to acetone and hydrogen cyanide. Although processing methods can reduce linamarin and cyanide in food, improperly processed cassava products would contain some amount of residual linamarin and hydrogen cyanide. This would result in the potential toxicity of the cassava products. Indeed, cases of cyanide toxicity from the consumption of inadequately processed cassava products have been reported [18, 25]. Recent studies have reported the presence of cyanogenic glycoside, amygdalin in cassava [14]. Amygdalin content of 8.84–48.33 mg/g has been reported to be present in cassava roots, depending on variety [14]. Bitter cassava varieties are more drought resistant and thus more readily available and cheaper but contain high level of cyanogenic glucosides. However, owing to food shortage in times of drought, less time is available for the additional processing required for cassava products. This leads to cassava products with high cyanogenic level with the potential of affecting consumers' health. Increasing the production of cassava breed with low cyanogen content [10] will improve healthy livelihoods of cassava producers, processors and consumers.

2.2. Cocoyam

Edible cocoyam is a nutrient dense tuber crop that belongs to Araceae family. Two major species of this family are Taro (*Colocasia esculenta* L) and Tannia (*Xanthosoma Sagittifolium* L). These species are commonly grown in the tropical region of Africa and are generally referred to as cocoyam [26]. Cocoyams are valued for its corms, cormels, and leaves. It can be converted into flour and used to make mashed meal or porridge; it can be consumed baked or boiled. It is a rich source of calorie for millions of people in the tropical and subtropical regions due to its high carbohydrate content [26, 27]. In addition to carbohydrate, cocoyam also contains other sources of nutrients such as protein, vitamins, carotenoids and minerals [9]. Apart from the nutrient composition of cocoyam tuber, the crops have been reported to contain low levels (2.10–17.13 mg/100g) of cyanogenic glycosides [28, 29]. In another study, cocoyam tuber was reported to contain 7.4 mg/100g equivalent cyanide [27].

2.3. Bamboo shoot

Fresh immature bamboo shoots are consumed as vegetable in some Asian countries. Bamboo shoot contains appreciable quantities of vitamin C, carbohydrates, and protein [30]. Besides its nutritive value, bamboo shoots also contain lethal concentration of cyanogenic glycosides. The cyanogenic glycoside present in bamboo shoot is taxiphyllin, which is decomposed quickly in boiling water. Cyanide content of bamboo shoot ranged from 1000 to 8000 mg/kg hydrogen cyanide [5, 31]. Although cyanide content of bamboo shoot is much higher than that of cassava root, the cyanide content in bamboo shoots decreases substantially following harvesting and processing [32].

2.4. Sorghum (*Sorghum bicolor*)

Dhurrin is the major cyanogenic glucoside in sorghum, representing 30% of the dry weight of shoot tips of seedlings, in addition to amygdalin [14]. In young sorghum leaves, dhurrin is localized in vacuoles of plants and the enzymes responsible for its hydrolysis to hydrogen cyanide is located in cytoplasm. In intact leaf, tissues are free from cyanide due to compartmental separation of the enzyme and the substrate. Concentration of dhurrin decreases as plant ages, immature sorghum leaves contains high concentration of dhurrin [33]. The cyanide content of sorghum increases rapidly during early growth stage, after which it declines with plant age [34]. The reports by [35, 36] confirmed the cyanogenic glucoside content in the tip of young seedlings of *Sorghum bicolor* that reaches 6% of the dry weight. Sorghum grains have been reported to contain 122.31 mg/g of amygdalin [14].

2.5. Fruits and fruits kernels

The most common cyanogenic glycoside in fruits and fruit kernel is amygdalin. Amygdalin contents of the fruit seeds vary significantly from seed to seed [13, 14, 37].

2.5.1. Apple (*Malus domestica*)

It is the most cherished fruit among the Rosaceae family. Apples can be consumed raw or processed into alcoholic (cider) or nonalcoholic beverage (apple juice) or apple sauce. Although apples are rich sources of vitamins and other nutrients, apple seeds contain high levels of cyanogenic glycosides. Amygdalin content of apple seeds ranged from 1 to 4 mg/g while that of apple juice was reported to be between 0.001 and 0.08 mg/ml [13, 37].

2.5.2. Apricot fruits (*Prunus armeniaca*)

They are cultivated in the Middle Asia, Africa, America, and Europe. The fruits are consumed raw or used in dry form for confectioneries while the kernels are usually processed before consumption. Apricot kernels are of two varieties; bitter and sweet. Bitter apricot kernels contain high amount of the cyanogenic glycosides, amygdalin, which can cause cyanide toxicity problems at high dose and thus, unsafe for consumption. Sweet apricot kernels as well as apricot flesh are safe for human consumption because of their low level of cyanogens [13, 38]. The concentration of hydrogen cyanide in Apricot kernels varies widely (49–4000 mg/kg),

depending on whether skin on or off varieties is surveyed. Cyanide level of raw or improperly processed apricot kernels can cause serious acute problems that could lead to death [4, 3]. Studies have shown that apricot kernel contain cyanide (CN) content of 1450 mg/kg, approximately 0.5 mg CN/kernel [39]. This value is similar to the toxic dose of cyanide (0.5 mg/kg body weight) reported by [5].

3. Health implications of cyanogenic glycosides

The toxicity of cyanogenic glycosides and their derivatives is dependent on the release of hydrogen cyanide. Toxicity may result in acute cyanide poisoning and has also been implicated in the etiology of several chronic diseases [7]. Dietary exposure to elevated levels of some cyanogenic glycosides in food has the potential to cause acute cyanide poisoning or a debilitating irreversible neurological condition in the long term.

3.1. Konzo

High and sustained cyanogens intake at sublethal concentrations from cassava or cassava flour in combination with a low intake of sulfur amino acids has been reported to cause Konzo in women and children [32]. Konzo is an upper motor neuron disease characterized by irreversible but nonprogressive symmetric spastic paraparesis that has an abrupt onset. It mostly affects children and women of childbearing age [40–42].

3.2. Tropical ataxic neuropathy (TAN)

It is another health problem associated with continuous consumption of improperly processed cassava products. TAN is used to describe several neurological syndromes attributed to toxiconutritional causes. TAN has occurred mainly in Africa, particularly Nigeria [43] and is common among people of 40 years and above [32]. Dietary exposure to cyanide from the monotonous consumption of inadequately processed cassava products over years is responsible for the cause of the disease. Symptoms of TAN include sore tongue, optical atrophy, neuro sensory deafness, and sensory gait ataxia [43].

3.3. Goiter and cretinism

They are common diseases in developing countries due to low intake of iodine (<100 µg/day). The disease is particularly common in Africa because of their over dependent on cassava as a staple food. Continuous exposure to dietary cyanide from insufficiently processed cassava products aggravate the disease [44] by the interferences of thiocyanate (the end products of cyanide detoxification in human system) with dietary iodine, thus leading to iodine deficiency. According to reference [44], populations with very low iodine intake and high thiocyanate levels from consumption of cassava, showed severe endemic goiter, which decreases with iodine supplementation. Study has shown that consumption of cyanogenic glycosides even at a very low concentration can also cause iodine deficiency leading to goiter [45].

3.4. Growth retardation

It is a common health problem especially among children in developing countries. Exposure to cyanogenic glycosides has been a contributing factor to this health problem. Growth retardation is particularly a serious problem in populations consuming foods with inadequate proteins especially diets that are low in sulfur containing amino acids (methionine and cysteine). This is because detoxification of cyanide in human body requires sulfur donors from sulfur-containing amino acids [46]. Thus, dietary exposure to cyanide is a contributing factor to growth retardation [47].

3.5. Cyanide poisoning

Cyanide toxicity occurs when cytochrome oxidase a_3 inhibits the terminal enzyme in the respiratory chain and halts electron transport and oxidative phosphorylation (which is essential to the synthesis of adenosine triphosphate (ATP) and the continuation of cellular respiration) [48, 49]. Cyanide poisoning occurs as a result of consumption of bitter cassava, almond kernels, or apricot kernels and their products without proper processing. Cases of cyanide poisoning after consumption of drink produced from the blends of apricot kernels and orange juice have been reported [50]. Clinical symptoms of cyanide toxicity are vomiting, nausea, dizziness, stomach pains, weakness, headache, diarrhea, and occasionally death [4, 51–54].

4. Effect of processing on cyanogenic glycosides

Processing methods, such as peeling, drying, grinding, soaking, boiling or cooking, soaking and fermentation have been reported by several studies to cause significant reduction in the cyanogenic glycosides of processed foods. These processes have been applied to food crops such as roots, tubers, cereals, and leaves, to cause significant reduction in the cyanogen contents of the crops. Food-processing methods generally disintegrate cyanogens contents of plants, and this leads to the production of cyanide. Since cyanide is volatile, further processing techniques, such as roasting and drying, will volatilize the remaining cyanide to low level.

4.1. Effect of soaking on cyanogenic glycosides

Soaking of cassava root has been reported to decrease its total cyanide content by 13.52% after 24 h, 73–75% after 48 h and 90% after 72 h [55]. Ref. [56] reported that endogenous β -glucosidase activity causes a significant degradation of amygdalin in ground apricot kernels soaked at 20°C.

4.2. Effect of fermentation on cyanogenic glycosides

Fermentation of cassava pulp or dough for 4–5 days has been reported to decrease its total cyanide by 52–63% [55]. Soaking and fermentation of bitter apricot kernels decreased cyanogen levels by about 70% [57]. The cyanide content of cocoyam flour produced from fermented

cocoyam was reported to reduce by 98.6% [27]. Prasad and Dhanya [58] reported a 84.6% reduction in the cyanide content of fermented sorghum leaves.

4.3. Effect of storage on cyanogenic glycosides

When foods produced from cyanogenic plants are stored at room temperature ($35 \pm 2^\circ\text{C}$), cyanide contents of the foods volatilize due to its low temperature (26°C). Ref [59] reported a decrease of 50–64% in the cyanide content of a cassava product (gari) stored for 4 weeks at room temperature.

4.4. Effect of cooking on cyanogenic glycosides

Cyanogenic glycosides are generally water soluble. During cooking, significant amount of cyanogens are leached into cooking water. Several studies have reported increased reduction of cyanide in cooked products. Steaming of a cassava product (akyeke) was reported to result in a 74–80% reduction in total cyanide levels. “Garification”, a process whereby fermented and dried cassava mash is simultaneously cooked and dried in a shallow wok, resulted in a 90–93% reduction in total cyanide content. Optimal cooking conditions for the reduction of cyanide levels in bamboo shoots ($98\text{--}102^\circ\text{C}$ for 148–180 min) resulted in a 97% reduction in cyanide [31]. Generally, traditional African processes typically decrease the cyanide content of cassava by 97–>99%. Also when the cooking method chosen is heating under dry, heat or at low moisture contents, the intake of the cyanogen is limited to only small amounts.

4.5. Effect of drying on cyanogenic glycosides

The efficiency of cyanide removal during drying is dependent on moisture content of the roots, rate of moisture loss (which relates to drying conditions), and the extent of tissue disruption of the plant tissue [60]. Extending the period of drying with higher moisture levels would enhanced linamarin breakdown, thus explaining the fact that fast drying rates result in lower detoxification, while slower rates result in higher cyanogen removal. Famurewa and Emuekele [61] reported that the higher moisture contents of the cassava root the greater the loss in cyanide content during drying. cutting of cassava tubers into small chips might create easy access for contact between the enzymes and cyanogenic glycosides resulting in higher hydrolysis. Reduction in cyanide content could also be as a result of variety, maturity and product sizes [62].

5. Cyanide detoxification in human

Cyanide is detoxified in the body by the enzyme rhodanase with the help of sulfur-containing amino acids to thiocyanate, which is excreted in the urine [63]. However, the detoxication mechanism of cyanide in the human body can only cope with low level of cyanide generated from consumption of small amount of cyanogenic plants.

6. Conclusion

Cyanogenic glycosides are abundant in edible plants. Consumption of improperly processed cyanogenic plants can lead to chronic and acute health problems. Understanding the appropriate processing methods for specific cyanogenic plants will help in reducing the problem of unintentional cyanide toxicity. Similarly, to prevent adverse effects of cyanogenic glycosides in food plants, consumers should prepare foods properly before consumption. It is recommended that cyanogenic plants should be cut into smaller pieces and cook thoroughly to release toxic hydrogen cyanide before consumption in order to reduce the level of the toxin. Also, seeds of fruits to be processed into juice should be removed before crushing to avoid cyanide poisoning.

Author details

Islamiyat Folashade Bolarinwa*, Moruf Olanrewaju Oke, Sulaiman Adebisi Olaniyan and Adeladun Stephen Ajala

*Address all correspondence to: ifbolarinwa@lautech.edu.ng, islamiyat202@yahoo.co.uk

Department of Food Science and Engineering, Ladoke Akintola University of Technology (LAUTECH), P.M.B. Ogbomoso, Oyo State, Nigeria

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