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Determination of cyanogenic glycoside linamarin in cassava flour using liquid chromatography-tandem mass spectrometry

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Abstract

A specific and reliable method was developed for determining the presence of linamarin, a cyanogenic glucoside in cassava flour and cassava starch, using liquid chromatography-electrospray ionization tandem mass spectrometry. Linamarin was extracted with acetonitrile and then purified by solid-phase clean-up using an NH_2 cartridge column. Isocratic HPLC was used to introduce samples for electrospray negative ionization tandem mass spectrometry. The multiple reaction monitoring (MRM) was performed using a characteristic fragmentation (*m/z* 246.1 → *m/z* 161.0) for linamarin. Calibration with a standard solution was linear over a working range of 0.001-0.1 ppm (r^2=0.995-0.999), which is equivalent to 0.18-18 μg/g in food samples. The mean recovery of linamarin from cassava flour was approximately 92-100%. The detection limits of the proposed method of linamarin in cassava flour and tapioca samples were 0.75 μg/g and 0.84 μg/g, respectively.

Keywords : cyanogenic glycoside, linamarin, cassava, tapiok, liquid chromatography-tandem mass spectrometry

I Introduction

Linamarin (phaseolunatin or acetone cyanohydrin-β-D-glucoside) (Fig 1.) is one of the major cyanogenic glucosides and toxic components found in many plants and is especially present in *Manihot utilissima*, also called cassava.[1, 2] The starch of cassava is consumed as a foodstuff worldwide. Owing to the toxic nature of linamarin, analytical methods have been developed for specifically monitoring linamarin as a means of regulation worldwide. Conventional analytical methods for linamarin detection based on its cyanide structure have used spectrophotometry, following endogenous enzymatic hydrolysis by β-glucosidase.[3-7] However, these methods involve time-consuming clean-up steps, making them inapplicable for processed foods such as cassava flour, as endogenous β-glucosidase could be removed or denatured during processing. Some studies have also analyzed linamarin as a cyanogenic glucoside using the post column high-performance liquid chromatography[8] and gas chromatography-flame ionization detector.[9, 10] However, as pretreatment for these methods is complicated, a simpler method is needed. In fact, quantitative and qualitative confirmation of linamarin contamination using reliable methods is necessary for regulation by governmental

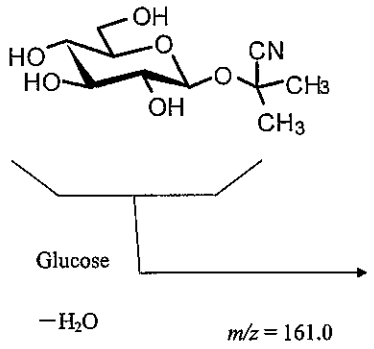

Fig. 1. Chemical structure and product ion of linamarin

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